Electrode and Interface Design for Lithium/Sodium – Selenium Batteries

by

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Abstract

Electric vehicles (EVs) have become a global trend to decrease fossil fuel use in transportation and reduce greenhouse gas emissions. The battery technology is one of the most critical parts of the wide adoption of EVs. The rapidly developing market for the emerging plugin hybrid vehicle and mobile electronics has prompted the urgent need for rechargeable batteries with high energy density. Although considerable progress has been made in lithium-ion batteries (LIBs), the overall energy density of LIBs is limited by the low capacity of current cathode materials. Therefore, cathode materials with high specific capacity have been extensively investigated. Selenium (Se) has drawn much more attention to be a good candidate in lithium/sodium batteries. Preparation of high-performance electrodes with tremendous capacity and durability over long cycling is the most challenging task. In this thesis, microporous carbon (MPC) derived from metal-organic frameworks (MOF) and polyvinylidene fluoride (PVDF) has found to be a suitable matrix to confine selenium and prepare Se-based cathode (MPC/Se), demonstrating high electrochemical performance in terms of cyclability, specific capacity, energy density, and rate capability. The polyselenides dissolution phenomenon in the Se-based batteries (shuttle effect), which was one of the most challenging parts, has been remarkably suppressed by using the optimized carbonization temperature (800°C), composite selenium content (50 wt.%), and electrode selenium loading (2 mg cm⁻²). The optimal MPC/Se cathode delivered a reversible capacity of 530 mAh g⁻¹ at a current density of 0.1 C in Li-Se batteries. Further studies showed that by the addition of a 3 vol.% fluoroethylene carbonate (FEC) additive to the electrolyte, a stable solid electrolyte interface (SEI) layer is formed on both cathode and the metal anode, enhancing the electrochemical properties of Li/Na-Se batteries and removing the shuttle effect issue. Further cathode development was conducted using the atomic layer deposition (ALD) technique to coat the electrode. The studies revealed that the five cycles coating of Alucone and Al_2O_3 could powerfully tackle polyselenide's dissolution into the electrolyte, resulting in high capacity and long life for Li/Na-Se batteries.

Lay Summary

Lithium/sodium-selenium (Li/Na-Se) batteries are promising energy storage systems among available technologies and play a critical role in portable devices, electric vehicles, and large-scale stationary energy storage due to their relatively high energy density and low cost. However, these batteries' practical application has been hindered by some critical issues that arise from the battery system, including cathode and electrolytes. Different materials and interface engineering approaches were developed in this work to overcome the challenges and improve the electrochemical performance of Li/Na-Se batteries. The effect of the carbon matrix, selenium content, and electrolyte additive was first investigated in capacity performance. The optimized cathode was improved by surface enhancement using the atomic layer deposition (ALD) technique and employed in Na/Se batteries.

Preface

All chapters in the thesis are based on work conducted in UBCO's Advanced Materials for Energy Storage Laboratory by Mohammad Hosein Aboonasr Shiraz under the supervision of Dr. Jian Liu. A part of chapter 3 (preparation of ZIF-8) has been done in Northern Analytical Laboratory Services (NALS) at the University of Northern British Columbia, Prince George, British Columbia. During the whole experiments in the thesis, I was responsible for all sample preparation and data analysis. My supervisor, Dr. Jian Liu, and the committee member were mentoring and leading me through the thesis direction. A list of any publications arising from work presented in the thesis and the chapters in which the work is located are as follows:

- Chapter 4: "Activation-free synthesis of microporous carbon from polyvinylidene fluoride as host materials for lithium-selenium batteries" <u>Mohammad Hossein Aboonasr</u> <u>Shiraz, Hongzheng Zhu, Yulong Liu, Xueliang Sun, Jian Liu.</u>, Journal of Power Sources, (2019)
- Chapter 5: "High-Performance Sodium-Selenium Batteries Enabled by Microporous Carbon/Selenium Cathode and Fluoroethylene Carbonate Electrolyte Additive" <u>Mohammad Hossein Aboonasr Shiraz</u>, Peter Zhao, Jian Liu., Journal of Power Sources, (2020)
- Chapter 6: "Nanoscale Al₂O₃ Coating to Stabilize Selenium Cathode for Sodium-Selenium Batteries" <u>Mohammad Hossein Aboonasr Shiraz</u>, Hongzheng Zhu, Jian Liu., Journal of Materials Research, (2019)

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Chapter 1: Introduction

Nowadays, energy storage is one of the top-rated concerns to increase deployment worldwide to suppress the enormous demand for fossil fuels and the emission of CO_2 . Due to growing environmental pollution concerns caused by non-renewable energy sources, more advanced renewable energy storage devices need favourable cycle life and suitability in electric and hybrid electric vehicles. Thus, both Li and Na ion batteries have been developed to compensate for this tremendous amount of demand.

A battery is a device that converts the chemical energy contained in its active materials directly into electric power using an electrochemical oxidation-reduction (redox) reaction. Typically, there are several major components in a battery cell consist of (1) the cathode, or positive electrode-the oxidizing electrode-which accepts electrons from the external circuit and is reduced during the electrochemical reaction, (2) the anode or negative electrode-the reducing or fuel electrode-which gives up electrons to the external circuit and is oxidized during the electrochemical reaction and (3) the electrolyte-the ionic conductor-which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalis to impart ionic conductivity.

For advanced rechargeable batteries, lithium-ion batteries and sodium-ion batteries are considered among the most promising candidates for electric vehicles, uninterruptible power sources, renewable energy sources, and storage due to their high energy density and low cost. The first report of sodium-based batteries backs to the 1970s, and research on lithium-based batteries [1-3]. However, in the 1990s, commercial lithium-based batteries are the proven candidates with market winning performance strategy to deliver the energy demand for hybrid electric vehicles. Thus, sodium batteries have been neglected [4, 5]. Because of lithium-ion batteries' low energy density, the state-of-the-art lithium-ion batteries cannot meet the increasing energy demand for next-generation electric vehicles (500 km drive range). Going beyond lithium-ion batteries' horizon is an incredible challenge that requires exploration of novel chemistries and novel materials.

Currently, lithium-sulphur (Li-S) batteries have shown the potential to provide 2-5 times the energy density of conventional lithium-ion batteries. However, the Li-S battery has still not reached mass commercialization, even after decades of research and development. This is due to its insulating nature and the dissolution of intermediary polysulfides into the electrolytes, and the volume change that occurs during the conversion of sulphur to Li₂S. Elemental selenium, a delectron-containing member in the same elemental group as oxygen and sulphur in the periodic table, has recently been proposed as the cathode material for rechargeable batteries. Comparable theoretical volumetric energy density, higher electronic conductivity, and selenium loading in the electrode make the selenium be expected a promising candidate that can provide a high volumetric energy density similar to sulphur while overcoming some limitations of sulphur [6-9].

Restrictions in lithium-ion batteries make the usage of these batteries with some problems [10-12]. Sodium-ion batteries make an alternative chemistry way for this great demand. Nowadays, sodium-ion batteries have been highlighted again among the most promising candidates for electric vehicles, uninterruptible power sources, renewable energy sources, and storage due to tremendous advantages such as being environmentally friendly, relative abundance, and low cost [13, 14]. Thus, sodium-based batteries can be used as an alternative candidate instead of lithium-based ones.

The common element in these battery systems is the electrolyte, which is in direct contact

with active materials and anodic metal (Li/Na), playing an essential role in transporting metal ions between the cathode and anode. Once the cathodes and anodes were determined in a battery system, the electrolyte would be the next functional factor that should be considered. By growing the cathode materials' potential capability in delivering high gravimetric capacity, finding the suitable electrolyte for the cell seems to be necessary. The liquid electrolytes are found to be practical in these battery systems, and further studies are needed to find the approach way into these electrolytes. Using the proper electrolyte in the cell, suppressing the formation/dissolution of intermediates, as renowned with the name of "shuttle effect", is applicable. The shuttle effect is one of the most common problems in these battery systems, and so many efforts have been made to remove this undesirable phenomenon [15-18].

This research covers the areas mentioned above by preparing different carbon matrixes to provide a desirable structure and space for confining enough selenium loading, good ion transfer, and electron conduction while maintaining high gravimetric capacity and avoiding the dissolution of active material (selenium) into the electrolyte. Different carbonization temperatures and selenium loadings were investigated in the next step to reach the optimized composite combination in Li-Se batteries. Once the composite-electrode configuration was well defined, the electrode's interface interaction has been investigated in the next step using different electrolyte additive contents. The effect of the solid electrolyte interface (SEI) formation derived from electrode-electrolyte interaction was studied on the electrolyte was then suppressed by introducing the Al₂O₃ coating with Atomic Layer Deposition (ALD) technique on the electrode surface. Various coating thicknesses were employed to reach the higher and more stable capacity in the Na-Se batteries. The thesis investigates the technical approaches to the electrode and

interfaces design and strategy in Li/Na-selenium batteries. Eliminating the polyselenide's dissolution is a challenging task that can easily accomplish if they accompany specific cathode designs and structures. This work opens a window for researchers to understand the concepts beyond lithium/sodium-selenium batteries.

1.1 Lithium-ion batteries

Rechargeable lithium-ion batteries are critical power sources for portable electronic device applications and large-scale stationary energy storage. The lithium-ion battery is the most successful of the possible electrochemical energy storage systems introduced during the 1960s and 1970s. The focus was on lithium metal as the anode because of its high specific capacity (3862 mAh g⁻¹). The mechanism in this type of battery has been depicted. In 1991, the first lithium-ion batteries marketed by Sony utilized petroleum coke carbon as an anode (180 mAh g⁻¹). After the first commercial product was introduced to Sony's market, lithium-ion batteries have become an essential requirement of everyday life because of their importance in all portable electronic devices. In the Mid-1990s, most lithium-ion batteries utilized electrodes employing graphitic spheres, particularly MesoCarbon MicroBeads (MCMB) carbon. A wider variety of carbon types have been used in negative electrodes of lithium-ion batteries. Since 2008, the search for new-generation anode and cathode materials to enable higher-performance lithium-ion batteries (350 Wh kg⁻¹ - 500 Wh kg⁻¹) is still in progress.



Figure 1. Li-ion batteries - working mechanism [19]

Conventional lithium-ion batteries based on traditional-metal-oxides cathodes (e.g., $LiCoO_2$, $LiMn_2O_4$, $LiFeO_4$, *etc.*) and graphite anode with low theoretical specific energy density cannot meet the crucial demands in electric vehicles, plug-in hybrid vehicles, and grid energy storage. Although lithium-ion batteries can be scaled up for electric vehicles or household energy storage, other alternatives seem more practical; hence, considerable attention has been paid to similar cells such as Li-sulfur and lithium-air batteries. These cells can have a similar reaction at the anode side, compared to the lithium-ion batteries, but the cathode undergoes a reactive or catalytic reaction. Therefore, the cell design might be different because of the harmful cathodic products, which should be separated from the anode half cell. While a lithium-air battery is based on an open system, a Li-sulfur battery is more similar to lithium-ion batteries.

1.2 Li/Na-sulfur batteries

Recently, sulphur-based batteries have drawn much more attention to renewable batteries. The high theoretical gravimetric (volumetric) energy density of 2570 Wh kg⁻¹ (2200 Wh L⁻¹) and low cost of that are two major factors contributing to its high demand [17, 20]. However, sulphur cathodes face different major challenges, which limit their practical applications: sulphur has a low electronic conductivity, which arises from its insulating nature cause low rate capability of this cathode: furthermore, large volume change during lithiation/delithiation or sodiation/desodiation make using this active material with some restrictions. Besides, during the charge and discharge process, high-order polysulfide intermediates are generated and dissolve in carbonate-based electrolytes, a process known as the shuttle effect [17, 21, 22].

The shuttle effect is one of the most common issues due to the non-conductive nature of elemental S_8 . It is necessary to dissolve S_8 so that high-order polysulfides can move forward with the lithiation/sodiation process. These high order polysulfides will face two different destinies, they can either diffuse to and react with Li/Na anode and form the low order polysulfides, move

back again to the cathode side or they will form some insoluble Li_2S and Li_2S_2 layer on the Li and increase the resistance of anode, the same pattern could happen for sodium anode as well. All of these cause a dramatic loss of sulfur during cycling resulting in a rapid decrease in coulombic efficiency and cycle stability of sulfur cathodes [23]. Making the cell stable over cycles is one of the most important things in battery design. By using the sulfur as active material in the cathode, fading the capacity is inevitable. Coulombic efficiency is another consideration that should take into account in this case.



Many different approaches have been investigated to address these problems. For instance, confining sulphur in microporous carbon is one of the most valuable strategies. Guo *et al.* prepared the microporous carbon matrix and achieved superior performance. Hippauf *et al.* demonstrate the comparison between microporous and mesoporous carbon host in Li-sulphur batteries' performance [25, 26]. The dissolution problem could be solved by confining sulphur in a porous matrix by either physical or chemical methods [27, 28]. However, sulphur still suffers from inevitable problems arising from its chemical nature. It was where finding another replacement is necessary.

1.3 Li/Na-selenium batteries

Elemental selenium, a d-electron-containing member in the same elemental group as oxygen and sulphur in the periodic table, has been considered a promising cathode material for

rechargeable Li batteries, demonstrating many advantages of sulphur and even more than sulphur. Selenium, $\text{Argon}^{18} 4\text{s}^2 3\text{d}^{10} 4\text{p}^4$ is very similar to sulfur. It has two different allotropes, i.e., trigonal selenium (t-Se, thermodynamically stable phase) with a chain-like structure and monoclinic selenium (m-Se) with a Se₈ ring structure. In comparison to sulphur, selenium has a higher electronic conductivity of 1×10^{-3} S m⁻¹ for selenium vs. 5×10^{-28} S m⁻¹ for sulphur. They have a similar volumetric capacity (3254 mAh cm⁻³) for selenium compared to sulphur (3467 mAh cm⁻³). However, selenium has a much lower specific capacity (675 mAh g⁻¹ for selenium vs. 1672 mAh g⁻¹ for sulphur). As a result of these qualifications, selenium is adequate to work as a superior active material employed in the cathode for high-performance rechargeable batteries. In the current study, we employed selenium as an active material for investigating the Li and Na batteries performance.

1.4 The electrochemistry of Li/Na with Se

In the search for a transformative new energy storage system, the rechargeable selenium battery systems have drawn much attention as cathode materials for the new generation of batteries due to selenium's high electronic conductivity and its high volumetric capacity. Li and Na's other electrochemical behaviour will be expected by employing selenium with different cathode structures, electrolytes, and electrode-electrolyte interfaces for rechargeable batteries. According to studies, the space-confined Se cathodes show a promising capacity performance with carbonate-based electrolytes. The shuttle effect and problems at the interface of electrode and electrolyte are also inevitable in this system. For replacing the Li with Na, economic and environmental advantages are applicable. On the other hand, low capacity and sluggishness in the charge/discharge reaction are the issues in developing high-power sodium-ion batteries. Therefore, a scientific study on the electrochemical behaviour of Li and Na with selenium is necessary.

Xin *et al.* investigated the selenium conversion in Li and Na batteries, using cathode containing Se_x in microporous slits in carbon (Figure 3). They showed that Se's reaction mechanism as single-chain molecules with Li happens in a single-step, converting Se_x chains to Li₂Se. Other studies used the pair distribution function (PDF) analysis and showed the Li insertion/extraction mechanism. They showed that the pristine Se has a trigonal structure and then changes to the antifluorite-type Li₂Se phase. The reaction starts from the Se_x chain, not the ring one, because Se is thermodynamically stable as chains, and they are stable during electrochemical cycling. From the electrochemical point of view, the Se₈ rings are electronic insulating, and the chain structure is more active as they have two terminals to interact with anodic metal [17]. Li *et al.* investigated the lithiation and sodiation of selenium using in-situ transmission electron microscopy. They also concluded that the reaction moves toward a single-step with a phase transformation from single-crystalline Se to a Li₂Se.



Figure 3. Electrochemistry of a Li-Se_x battery: (a) energy (per electron) released in one-step lithiation of Se_x, (b) sectional view and a front view showing the Li⁺ migration in a Se_x preoccupied slit pore, and electrochemistry of (c) Cycle 1 and (d) Cycle 2 [29].

Na and selenium's reaction (Figure 4), continuous chain shortening of Se_x upon initial discharge happens to yield highly active small Se molecules and finally converts to Na₂Se. The slit size of the carbon substrate for the Se chain should be in a way not impede the Na⁺ migration yet provide improved trapping of the active metal. Na+ migration can be better to enlarge the carbon pore size so the kinetics upon sodiation/desodiation can be guaranteed [29]. Similar results were found in Li *et al.* works that selenium has alloying reactions with both Na and Li. The three-step reaction occurs: first, the transformation of selenium into amorphous phase Na0.5Se happens and then converts to the polycrystalline Na₂Se₂ phase and finally transforms to Na₂Se phase. The reaction kinetics of sodium is 4-5 times greater than that of lithium. The solid-state amorphization process is ten times higher as the Na-based intermediates have high electronic conductivity and ionic diffusivity. They found their results according to their density functional theory calculation and by in situ TEM investigation [30].



Figure 4. Electrochemistry of a Na-Se_x battery in Cycle 1: (a) energy (per electron) released in stepped Na intercalation of Se_x, (b) Na⁺ migration in a Se_x preoccupied slit pore, and (c) electrochemistry of Cycle 1 [29].

1.5 Electrolytes for Li/Na-Se batteries

Liquid electrolytes are favourable due to their low surface tensions and low viscosities. Liquid electrolytes are highly conductive and have been used to improve the performance of rechargeable batteries. An advantage of the liquid electrolyte can be a good contact of cathode and electrolyte, providing lower resistance and better ion diffusion in the solution. However, the shuttle effect diminishes the actual potential usage of them in Li/Na rechargeable batteries. It leads to lower Coulombic efficiency and the corrosion of metallic anode during prolonged cycling. Se-based cathodes' liquid electrolytes can mainly be categorized into two groups, etherbased electrolytes and carbonate-based electrolytes. The structural and name of common electrolyte solvents has been shown in Figure 5.

Ether		Carbonates		Sulfones		Ionic liquids	
Abbreviations	Structures	Abbreviations	Structures	Abbreviations	Structures	Abbreviations	Structures
DOL	~ \$ \$	EC	Å	EMS	~ %	Cations	
DME	~ ~~~ ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	DEC	\cdot	TMS	-4	pp ₁₃ +	stige.
G3	᠂ᡷᢦᡲᡒᡧᡷᢞᡓᠰᢩ᠅	DMC	Set a	DMSO	×	pp ₁₃ +	YY YY
G4	Stoff goglesgog	FEC	*			Pyr _{1.201} +	÷+19
THF	star s					Anions	
TTE	Xery.					TFSI-	yer.
BTFE	- fort					FSI-	×
DMDS	Same					CF ₃ SO ₃ -	20

Figure 5. Structural and name of common electrolyte solvents [31]

1.5.1 Ether-based electrolytes

The mechanism behind the lithiation of Li-Se battery in the ether-based electrolyte was investigated by Cui *et al.* by using in situ high-energy X-ray diffraction (HEXRD) and X-ray absorption spectroscopy (XAS) [32]. The in situ Se K-edge XANES measurement showed the formation of polyselenides during the cycling, and the reaction cannot be well interpreted with

only a two-phase transition mode. The two first and last phases of reaction materials, consisting of the Se and Li₂Se, cannot be dissolved in ether-based electrolytes, while the polyselenides have very high solubility. The mechanism in this electrolyte follows several steps in which Se is first converted to Li₂Se_n (n \geq 4) at 2.04 V and then reduced to Li₂Se₂ and Li₂Se after discharging to 2.06 and 0.8 V, respectively. The charging process's reaction is the conversion of Li₂Se to Li₂Se_n (n \geq 4) and then Se. In Se-based cathodes, the polyselenide intermediates are usually formed in ether-based electrolytes making several discharge plateaus related to Li₂Se₈ or Li₂Se₄ reduction [33-35].

Lower dissolution of the polyselenide and reaction with Li metal was also found in concentrated ether-based electrolytes. This can happen by increasing the Li salt in the electrolyte and using the highest Se usage rate in the cathode structure [36, 37]. Increasing the concentration of electrolytes has also been reported as a possible pathway to improve alkali metal ions' cycle life in ether-based electrolytes. Thus the solvent decomposition, transition metal dissolution, and Al current collector corrosion are all suppressed using the superconcentrated electrolytes [38-46]. Li salt's high concentration in the ether-based electrolytes exhibits superior performance in Li metal anode and Na metal plating/stripping reaction [47-50]. Several studies showed that the SEI layer formed in ether-based electrolytes is more stable. However, the ether-based electrolytes can be easily oxidized at high potential, and also they are unstable on 4 V class cathode surfaces [51-53].

The discussed mechanism has made it necessary to design the host structures to be conductive and providing an excellent space to constrain the polyselenides and prohibit their solution into the ether-based electrolyte and causing the shuttle effect. Different carbon architectures have been employed as the matrix for Se-based cathodes in ether-based electrolytes [9, 27, 54-60]. Babu and Ramesha showed that by encapsulating the Se into the host, the direct conversion mechanism could also occur in ether-based electrolytes [61]. Han *et al.* found that using reduced graphene oxide coating on the Se/mesoporous carbon particles, the dissolution of intermediaries can be significantly suppressed, resulting in better cycling stability of Se cathode in ether-based electrolytes [56]. Fang and their group used a graphene-coated separator to prevent the shuttle effect in ether-based electrolytes for Se-based cathodes [62].

1.5.2 Carbonate based electrolytes

The alkyl carbonate solvents can be divided into two main groups, linear carbonates and cyclic carbonates. Each group contains different solvents. For example, for linear carbonates, ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) are the most common ones. In contrast, for the cyclic group, ethylene carbonate (EC) and propylene carbonate (PC) can be used typically [63]. Carbonate-based electrolytes have been extensively applied in Li/Na/K rechargeable batteries, delivering higher safety and oxidation potential, more comprehensive electrochemical stability range, with lower cost and better conductivity [64].

The carbonate electrolytes shift the reaction mechanism towards the one/single step, producing the reduced selenium without forming polyselenides intermediates in Se-based batteries [65-69]. Wang *et al.* prepared a high-performance sodium-selenium cell by coupling a binder-free, self-interwoven carbon nanofiber-selenium cathode with a light-weight carbon-coated bifunctional separator. They showed that the single plateau is observed in 1M NaClO₄ EC-DMC electrolyte during the discharge-charge process related to the conversion of Se_n to insoluble Na₂Se [70]. The space-confined Se cathode materials could demonstrate excellent electrochemical performance in Li-Se batteries with carbonate-based electrolytes. The superior cycling performance in carbonate-based electrolytes could also be attributed to forming a solid-

electrolyte interface (SEI) layer, which prevents the Se cathodes from irreversible reaction with the carbonyl groups. The problem of carbonate electrolyte interaction with selenium can be addressed by using confining the selenium into the mesoporous carbon host. The Se-O layer created on the cathode acts as an SEI layer and protects the Li_x Se from further reduction. The carbonate-based electrolytes have attracted more significant attention because of Se cathode materials' performance [71]. The dissolution of polyselenide into the carbonate-based electrolyte can be suppressed by avoiding the nucleophilic attack of carbonyl groups as polyselenides are not dissolved in carbonate-based electrolytes. After the first cycle, the formation of the SEI layer is also helping the prevention of the shuttle effect, resulting in better electrochemical performance [71-74].

1.5.3 Electrolyte additives

The SEI layer formation could be elevated by employing some additive into the electrolyte such as fluoroethylene carbonate (FEC) or vinylene carbonate (VC), which provides a decomposition pathway rather than solvent/co-solvent decomposition to make a stable SEI layer on the surface of electrodes. For example, 5 wt.% FEC has been used as an electrolyte additive into the 1.0 M NaClO₄ propylene carbonate-ethylene carbonate electrolyte to form an SEI layer which is further confirmed by the elemental mapping analysis. This stable thin film could eliminate the shuttle effect and made the superior rate capability with a reversible capacity of ~390 and 127 mAh g⁻¹ at 0.1 and 5 A g⁻¹, respectively, in Na-S batteries [75]. FEC has also been found practical to improve the efficiency of metal anodes. Mogi *et al.* saw 5 wt.% FEC to the 1M LiClO₄ PC electrolyte increase the Coulombic efficiency of Li anode [76]. Ring-opening polymerization forms a stable surface film on Li metal through the electrochemical reduction in the discharge process [77-79]. Shiraz *et al.* investigated the effect of different FEC content

additives on the 1M NaClO₄ EC-DEC electrolyte working in sodium selenium batteries. They showed that by using the microporous carbon-selenium (MPC/Se) and 3 vol.% FEC additive in the electrolyte, a specific capacity of 382 and 350 mAh g^{-1} in the 100th and 200th cycle could be achieved, respectively. Simultaneously, the MPC/Se cathode without FEC could only deliver 317 and 245 mAh g^{-1} after 100 and 200 cycles, respectively. They found the effect of FEC additive on the stability of Na metal anode's morphology by decreasing the corrosion of metallic anode, resulting in high and stable electrochemical performance of the cell over long cycles in Na-Se batteries [80]. The mechanism behind the formation of SEI is the sacrificial reduction in which, the additive which has a higher reduction potential than that of solvent molecules/polymer or conducting sodium salts, reduced preferentially and make the parent electrolyte protected from further decomposition, leading to the formation of a SEI layer [81].

1.5.4 Comparison summary

Table 1 summarizes the advantages and limitations of the ether/carbonate-based electrolytes in the Se-based batteries. Table 2 provides more information on the electrochemical performance of space-confined Se cathodes in carbonate-based electrolytes.

Electrolyte	Advantages	Limitations
Ether based	Stable SEI layer, high ion transmission, low-viscosity, excellent wettability, dendrite-free electrochemical behaviour, less reactive, limited ionic conductivity	Severe shuttle effect, high oxidization, high volatility and high flammability, polyselenide formation and high polyselenide dissolution, multi-phase conversion, safety issues, strong self- discharge, low capacity, and fast capacity decay
Carbonate based	Better cycle stability, higher safety and oxidation potential, wider electrochemical stability range, lower cost, good conductivity, acceptable electrochemical stability, high ionic conductivity, wide operating temperature range, sufficiently low toxicity	Reactive with the metal anode

Table 1. Characteristics of electrolytes used for Se-based batteries.

Table 2. Electrochemical performance of space-confined Se cathodes in carbonate-based electrolytes.

Materials	Se loading, %	initial capacity, mAh/g	last capacity, mAh/g	cycles	rate, mA/g	Ref.
Se/PAN-CNT	35	~400	517	500	500	[69]
carbon nanofibers/Se composite	52.3	~600	516	900	500	[82]
Se/microporous carbon	60	664	506	150	675	[83]
Se/PTCDA-derived carbon	54	560	430	250	100	[66]
Se/porous carbon sponges	50	471.6	443.2	200	337.5	[84]
Se@N-doped MPC	50	460	460	1600	1350	[85]
Se-confined microporous carbon	51	341	249	3000	675	[86]
Se/MPCS	60	660	540	100	67.5	[87]
Se/microporous carbon spheres	70.5	656	416	1200	675	[88]
Se/CMK-3 composite	49	670	600	50	67.5	[89]
Se/mesoporous carbon spheres composite	30	480	~500	1000	168.75	[90]

1.6 The electrode-electrolyte interface

In Se-based electrodes, the solvent/co-solvent of carbonate-based electrolytes can directly react with the selenium to crate the solid electrolyte interface (SEI) protecting layer. This stable

solid phase generates on the cathode surface, making it much more stable over cycles, resulting in better electrochemical performances by suppressing the formation/dissolution of the polyselenide into the electrolyte. This layer must be durable and absorbent enough as a basic requirement for the cell's long-term stability [72, 91]. The formation of the SEI layer is not limited to the cathode side of a battery system. The interaction of anode and electrolyte plays a vital role in any type of battery. The SEI could form via the reaction between electrodeelectrolyte, organic solvents, and metal salt [63, 92]. This interaction usually creates an SEI film on the surface of cathode/anode electrodes, making the proprieties dependent on it (Figure 6). With a compatible electrolyte structure, so many advantages such as higher capacity and Coulombic efficiency, longer cycle life, electrochemical stability derived from the suppression of intermediates dissolution into the electrolyte could achieve in all Li/Na based batteries [93, 94].



Figure 6. Elemental mappings and demonstration of SEI formation on Se/PCNs after one cycle [95].

Yang *et al.* reported that the nucleophilic nature of polyselenides, makes them reactive with the carbonate-based electrolytes. Therefore, Se cathodes' stability in carbonate-based electrolyte could be attributed to the protection that happens by the spatial confinement of Se and passivated SEI films. In other studies, the formation of SEI film has been identified by ex-situ TEM observation, X-ray photoelectron spectroscopic (XPS), and electrochemical impedance spectroscopy (EIS) analysis [32, 72, 87]. Several reports based on selenium electrodes and different battery systems employed the carbonate-based electrolytes and showed the catalytic formation of SEI on the fracture surfaces of active materials and anodic metal such as Na/Se

batteries with 1M NaClO₄ EC-DMC electrolyte; [96]. The SEI film plays crucial roles, precluding the polyselenides (if any) from dissolution into the electrolyte; make it much more stable over cycles in carbonate-based electrolytes [91, 95].



Figure 7. Schematic illustration of the proposed strategy for Se cathode stabilization and solid electrolyte layer in situ formed both within the pores remaining after Li_2Se formation [91].

1.7 Selenium-based cathode structures

Active metal and its carbon matrix host in cathode structure are the critical components in determining the electrochemical behaviour of Li/Na rechargeable batteries with carbonate-based electrolytes. Several studies have shown the suppression of the creation or dissolution of intermediates into the carbonate-based electrolytes by manipulating the active metal size and structure or carbon support pores and chemical characteristics.

1.7.1 Active metal size

The effect of the active metal molecular structure was investigated in Li-Se batteries with carbonate-based electrolytes to remove the formation of polyselenides intermediates. Luo *et al.*

worked in this, where the cyclic-Se₈ was infiltrated into the mesoporous carbon sphere at 600 °C under vacuum. The electrochemical test showed that by impregnating the Se into the mesopores of carbon at high temperature and using low-cost carbonate-based electrolyte of LiPF₆ EC/DEC, polyselenide dissolution successfully suppressed and this could happen by the existence of chain-like Se molecules in the mesoporous carbon sphere after the first charge process. The Se₈/mesoporous carbon composite cathodes delivered a reversible capacity of 480 mAh g⁻¹ for 1000 charge/discharge cycles without any capacity loss at 0.25 C and 46% of capacity retention at 5 C [90].

1.7.2 Carbon hosts

Some of the research on enhancing the electrochemical properties of the battery systems was focused on developing carbon support with a unique structure to hit the shuttle effect and suppress the dissolution of polyselenides into the electrolyte by trapping them inside the carbon matrix or providing a way for reaction mechanism to happen in one step phase during charge and discharge. For sulphur batteries, ether-based electrolytes are much practical than carbonate-based electrolytes, while polyselenides can be dissolved in ether-based electrolytes much higher than carbonate-based electrolytes. They form polyselenides in the ether-based electrolytes because of Se reduction into different intermediates and further decrease to Li₂Se₂ and Li₂Se during the discharge process. As a result, Se batteries' electrochemical performance and rate capability are more excellent in carbonate-based electrolytes as selenium is reduced to Li₂Se in one single step, showing one plateau without forming polyselenide intermediates. Like sulphur, Se is also subjected to volume expansion because there is not enough space to accommodate the Se structure's anodic metal insertion. Therefore, pure selenium cannot be used directly as a cathode. The researchers found that by using a porous carbon matrix as a Se host, there would be enough

space for metal interaction with selenium, moving the reaction in a one-step mechanism without the polyselenide introduction in the carbonate-based electrolytes. Based on the calculation, the sufficient micropore size to confine Se_8 molecules should be larger than 1 nm. The incorporation of carbon and active metal is one of the critical elements in determining the cathode performance. The carbon and active metal are in contact with each other.

1.7.2.1 Selenium-carbon melt diffusion

The insulating nature of electroactive metals associated with redox reactions has made it necessary to confine them into the electronic conductor host, mainly carbon. The characteristics of this carbon host have a direct impact on electrochemical performance. Dutta *et al.* used a pressure-induced capillary encapsulation protocol to confine selenium and sulphur inside carbon nanotubes (CNTs). They showed the confinement, lowered the surface tension of molten Se/S, introducing the high wetting and remarkable loading of the CNTs. Their S-CNT and Se-CNT composites showed high efficiency in the electrochemical reaction, related to the efficacy of the encapsulation protocol of S/Se inside the CNTs. They also confirmed the confinement of polyselenides/polysulfides within the CNT cavity precincts, resulting in the stability of rechargeable batteries over cycles [97].

The other studies worked with $S_{1-x}Se_x/C$ (x≤0.1) campsites, showed that by immobilizing the electro-active metals in porous carbon and the interaction of sulphur with selenium, the active material remarkably confined in the carbon host at 260 °C, resulting in restriction of the dissolution of Se/S cathodes during cycling. Therefore, high electrochemical performance in a carbonate-based electrolyte can be achieved by delivering the capacity of 910 mAh g⁻¹ at 1 A g⁻¹ over 500 cycles and 1105 mAh g⁻¹ at 0.2 A g⁻¹ after 100 cycles [74].


Figure 8. Schematic illustration of the synthesis process of MHPCS/Se composites [98].

1.7.3 Selenium-carbon chemical bonding

In addition to the carbon pore structure, its chemical functionality also plays a substantial role in preventing the penetration of intermediates into the carbonate-based electrolytes, causing the shuttle effect's suppression. The electrochemical activity of carbon can be further improved by the graphitization and alteration of the sp² hybrid. The charge across the sp² basal plane can be uniformly spread by doping the carbon with N, O elements. Hence the chemical interaction of carbon and polyselenide can be more vital to avoid the shuttle effect. For example, the Se molecules interactions can be more potent by the presence of a small amount of oxygen-based functional groups in the carbon structure. The strong C-O and Se-O groups in the composite material can enhance the electrode's mechanical and electrical performance, resulting in better hosting lithium [87, 99].

Ding *et al.* prepared selenium in cellulose-derived carbon nanosheets (CCNs), termed Se-CCN, and investigated its electrochemical performance in 1MNaClO₄ EC: DMC electrolyte. The melt diffusion made the carbon selenium composite of selenium into the carbon-derived cellulose nanocrystals at 260 °C followed by heating up to 600°C. Their XPS investigation demonstrates a shift of ~ 0.6 eV in the binding energy of elemental Se, showing the change in electron cloud density. They confirmed the chemical bonds between selenium atoms contacting CCNs [100]. The FTIR spectrum supported this chemical bonding, showing the Se-C stretch and bend characteristic peaks [96, 101]. According to Luo and their group report, by preparation of *in* situ carbonized perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) mixed with selenium in a sealed vacuum glass tube, Se will be chemically bonded by carbon. This makes the mitigation of the shuttle effect and suppression of polyselenide dissolution into the carbonate-based electrolyte. They supported their investigation by Raman spectroscopy showing the disappearance of cyclic Se₈ peak. The highly encapsulated and chemically bonded Se with carbon matrix, greatly enhances the charge/discharge cycling stability in both lithium and sodium batteries by delivering the capacity of 430 mAh g^{-1} after 250 cycles in Li-ion batteries and 280 mAh g^{-1} after 50 cycles in Na-ion batteries at a current density of 100 mA g^{-1} , respectively [66]. Sha et al. prepared a new self-repairing system in which the Se atoms chemically connected to the carbon matrix can anchor other Se atoms to attach the tails and create Se-Se- chains, avoiding the dissolution of intermediates into the electrolyte. They claimed that chain-like Se being successfully decorated on GE and formed Se-C chemical bonds because of the ball-milling process, ascertained with Raman and XPS analysis. This chemical bonding even enhanced selenium's thermal stability as the melting point was reached 450 °C in composite [102]. The above cathode structure enhanced by chemical bonding between Se and carbon could deliver an initial capacity of 1050 mAh g⁻¹ followed by a recovery to 92% of the original total, which is then maintained over 500 cycles Li-Se batteries [102].



Figure 9. Schematic illustration of the synthesis process for the Se@NCA electrode [103].

1.7.3.1 Selenium-carbon incorporation

Changing the active material size and carbon support structure/characteristic carbonatebased electrolytes would be efficient to eliminate the shuttle effect phenomenon, but incorporating active metal during the carbonization process is a practical approach to preparing composites with appropriate confinement and superior electrochemical performances. In Li-Se batteries, Zeng *et al.* prepared the PAN/F-127 nanofibers mats with the long and straight structure via the electrospinning technique, followed by carbonization and activation processes. The produced porous carbon nanofiber mats (PCNFs) with sufficient mesopores were used as a selenium host (Se@PCNFs), and the composite showed a high reversible capacity of 516 mAh g⁻¹ after 900 cycles without any capacity loss at 0.5 Ag⁻¹, with Coulombic efficiency of ~100% throughout the processes. The uniform distribution of Se in PCNFs and the 3D interconnected PCNFs framework could alleviate the shuttle reaction of polyselenides intermediates during cycling and maintain the perfect electrical conductivity throughout the electrode in the 1M LiPF₆ in EC-DMC electrolyte [82].

Carbon nanofibers (CNFs) incorporate active material in the cathode and are used as a capable electrode in sodium selenium batteries. A study done by Wang et al. self-interwoven CNF/Se electrode infiltrated Se into KOH activated porous carbon nanofiber coupled with a light-weight carbon-coated separator for Na-Se batteries. They showed highly reversible capacities of 599 mAh g^{-1} at 0.1C rate and 382 mAh g^{-1} at a 5C rate. The robust electrode structure could successfully suppress the polyselenide dissolution into the electrolyte. The 3D interconnected open channels significantly improve electron and Na ion accessibility, thus rendering high power density [70]. Zhang *et al.* could provide a facile way to incorporate Se with nitrogen and sulfur dual-doped hierarchical porous carbon with interconnected conductive polyaniline (PANI) coating (i-PANI@NSHPC/Se) to suppress the shuttling effect and the mitigation

of polyselenide from the cathode to the anode leading to dramatic capacity decay, severely impeding the Na-Se batteries practical applications. They confirmed the strong chemical affinity and physical diffusion barrier for polyselenide using Ex-situ characterizations Raman, XPS, SEM, and EDS mapping and density functional theory (DFT) calculations. The capacity of 617 mAh g⁻¹ after 200 cycles at 0.2C was achieved for this rationally designed structure of i-PANI@NSHPC/Se composite [104].



Figure 10. (a) Reaction mechanism and changes in the molecular structure during the carbonization of PAN and selenization between Se and c-PAN; (b) Possible molecular structures of the as-prepared chemically-bonded selenium/carbon composite [105].

1.8 Impact of battery technology on green house reduction in Canada

Most mid-century international and Canadian greenhouse gas abatement studies find that today's technology can make deep emissions reductions, although mitigation costs remain high in certain areas. For example, a 2015 assessment by the Council of Canadian Academies suggests that Canada can significantly reduce greenhouse gas emissions by using commercially available technologies in the economy's critical sectors. Studies consistently indicate that the technologies currently in use are essential components of the climate protection solution, such as the 40

expansion of non-emitting electricity in end-use industries and the increasing diffusion of alternative fuels and the improvement of energy-saving and efficiency.

On March 3, 2016, Canada's first ministers and indigenous leaders met in Vancouver and committed to developing a concrete plan to achieve Canada's international greenhouse gas reduction commitments through a pan-Canadian framework for clean growth and climate change. Canada's first ministers released the Vancouver Declaration. They agreed to build on promises and actions already taken by provinces and territories to meet or exceed Canada's greenhouse gas emissions targets. They stressed the need to encourage investment to foster clean economic growth and create jobs that support the transition to a low carbon economy while benefiting individual Canadians and addressing business competitiveness. They pledged to take mitigation measures by adopting a wide range of domestic measures, including carbon pricing mechanisms, adapted to each jurisdiction's specific circumstances. Commitments have also been made to develop and implement robust and complementary development. Adaptation policies and climate resilience measures to cope with climate risks for our population, infrastructure, economy and ecosystems and especially for the northern regions of Canada.

The private sector has been a leader in energy storage research. Battery storage technologies for cell phones, computers and electric vehicles have seen tremendous growth in recent years. Already now, lithium-ion batteries' cost is being reduced significantly through the production of electric transport companies such as Tesla Motors. Besides, other cheaper and more efficient options are being developed with opportunities for the whole energy sector. For example, battery technologies based on sulphur and graphene offer enormous potential for cheaper and more powerful battery storage systems. Other energy storage options are available, some of which have already been adopted by Canadian electricity companies. The Toronto

Hydro Company's pilot project for storing compressed air energy was recently carried out in Lake Ontario and now offers 1 MW of storage capacity that can be fed into the city network during peak load times. Thermal energy storage is also used in the Okotoks, Alberta community. However, some Canadian provinces' most promising option is likely to be pumped storage power (PSH). The technology is readily available, has low operating and maintenance costs, and is not limited by cycle degradation. While recent improvements in the private sector are encouraging, much more innovation is needed to enable widespread renewable energy production by 2050. Because of the essential role of energy storage technologies in many electrifying processes, including transport, it is fundamental that energy storage technologies continue to improve over time. To achieve this, governments and private actors have a shared responsibility to increase investment across the innovation chain to bring breakthrough technologies and incremental improvements to the market.

1.8.1 Electrified public transport and smart urban planning

In the transition to a low carbon economy, public transportation results in a significant reduction in greenhouse gas emissions than private vehicles, but diesel buses still emit a considerable amount. More recently, advances in the development of batteries for electric cars have shifted to city buses. For example, Gothenburg has used three electric buses on one of its public transport routes and has used seven hybrid electric buses. Although the buses are considerably more expensive to buy than diesel buses, the fuel savings quickly make up for this difference. The buses are charged for six minutes between trips, which gives more than enough range for the route they serve. At the same time, they offer sockets for charging phones and WiFi for users on the buses. Similar projects are ongoing in Montreal, starting with hybrid electric buses. Another vital aspect of moving to a low-carbon economy is planning and designing cities

to support low-carbon technologies and lifestyles and correct traffic congestion in major Canadian cities. Congestion is a significant cost to the economy, valued in 2008 as a direct and indirect cost to the Greater Toronto Area and Hamilton Region regional economies of \$6 billion per year. This type of structural change will take some time. Still, governments can start creating momentum in the short term by adopting a holistic development approach by integrating land use, transport, energy production and community planning. More and more cities are looking for innovative solutions to reduce traffic jams on their streets. For example, Edmonton is one of two Canadian cities participating in a North American program to develop connected vehicle technology. This technology can improve many traffic elements in cities by preventing collisions between cars, guiding drivers through detours if there is a slowdown or an accident on the road, and even adjusting traffic lights along detour routes to minimize congestion.

Other technological advances are leading to autonomous vehicles and greater use of vehicle sharing, which will have important implications for people's future movement within cities. Technological advances are also paving the way for a new management approach by cities and governments, such as efficient pricing for toll mechanisms. For example, the high-occupancy toll lanes allow both vehicles with enough passengers and owners to drive on these lanes, which allows for less congestion and revenue that can be invested in public transport.

1.9 Thesis objectives

Lithium/sodium-selenium (Li/Na-Se) batteries are promising energy storage systems and play a critical role in portable devices, electric vehicles, and large-scale stationary energy storage due to their relatively high energy density and low cost among available technologies. They can reduce humankind's reliance on fossil fuels and solve related environmental problems. However, the practical application of these batteries has been hindered by some issues such as limited overall performance, especially the low energy and power density, that arise from the battery system, including cathode and electrolyte. As Li/Na-Se battery performance is highly dependent on the choice of electrode materials and the reactions at the interface between electrodeelectrolyte, the design of new electrode/interface materials resulting in high theoretical specific capacities becomes a key step to obtain suitable Li/Na-Se batteries, which would exhibit higher energy density, better rate capability, and higher safety performance. In this context, this thesis research aims to develop Se/C cathode materials and design the interface to enable highperformance Li/Na-Se batteries. We did understand the working mechanisms and interplay between Se/C cathode and electrolytes in these battery systems.

Part 1: To synthesize carbon host for selenium

1) Develop microporous carbon from metal-organic frameworks (MOFs): Preparation of the unique carbon structure was the first step in studying. Carbon derived from direct carbonization of ZIF-8 chose to be a carbon matrix for burying the selenium, making carbon selenium composite. The microporous carbon/selenium composite has been prepared by the melting diffusion method, and the electrochemical performance of the fabricated electrode using the Se/CZIF composite was studied.

2) Develop microporous carbon from polyvinylidene fluoride (PVDF): To make a good comparison between different carbons and their performance in Li/Na-Se batteries, carbon 44

derived from PVDF was also investigated in the study. The best-performed carbon was then chosen and optimized in terms of carbonization temperature, and Se/C composite was studied on loaded selenium content and selenium loading on the electrode.

Part 2: To develop electrode-electrolyte interface interactions

3) Design and optimize electrolyte additives for Se/C cathode: The electrode's interface is directly connected with the electrolyte. Therefore, the electrolyte contents play an essential role in the final performance of the battery. In this objective, the main electrolyte components have been determined; the type of additive and its content are well optimized to reach the suitable electrolyte solution for use in Li-selenium and Na-selenium batteries.

4) Design and optimize the electrode surface coating to stabilize Se/C cathode in carbonate-based electrolytes: Atomic layer deposition technique was used to make a stable coating layer on the optimized surface electrode to stabilize Se/C cathode in carbonate-based electrolytes. Al_2O_3 and Alucone were employed as a coating agent to suppress polyselenide's dissolution into the electrolyte solution. Different ALD thicknesses were investigated to achieve the best capacity performance and rate capability in Li/Na-Se batteries.

1.10 Thesis organization

This thesis consists of 7 chapters: 1-introduction, 2-methodology, 3-6 results and discussion, and chapter 7-conclusion organized in an "Integrated-Article" format. Specifically, this thesis includes the following parts:



Electrode and Interface Design for Li/Na-Se batteries

Figure 11. Thesis structure and contribution between sections

Chapter 1-Introduction: gives a general introduction to lithium-ion batteries (LIBs) and the necessity of having higher energy density batteries such as Li/Na-Se batteries, challenges that existed in Li/Na-Se batteries for electric vehicles and hybrid electric vehicles, and the solutions offered by designing electrode and interface of such battery system. Moreover, the research objectives and the thesis structure are also stated clearly.

Chapter 2- Methodology: outlines the methods used to synthesize carbon materials as a selenium host and electrode/interface fabrication techniques, with the characterization methods

used to analyze the physical and electrochemical properties.

Chapter 3-6: Results and discussion:

Chapter 3: This chapter mainly discusses the first carbon synthesis approach employed as a selenium host in Li/Na-Se batteries. We use our chemistry and materials science expertise to develop high-performance Li/Se batteries for EV applications by materials innovation. To do so, preparation of carbon host is a must, which needs to be focused on different parameters such as the correlation between materials structure (especially pore size and volume) and battery performance, and provide guidelines for battery cathode design next steps. This chapter developed zeolitic imidazolate framework-8 (ZIF-8), a subclass of MOFs, as the microporous carbon source to build a Li-Se battery. The electrochemical performance of the electrode prepared with this carbon was investigated in both bare Se/CZIF and Alucone coated-Se/CZIF samples.

Chapter 4: This chapter is the next stage of the previous chapter, in which the carbon derived from ZIF-8 showed relatively stable capacity performance over cycles. However, to compete with recent advances in Li-Se batteries done so far, the Se/CZIF (coated and uncoated) could not fully meet the minimum requirements of electrochemical performances expected. Thus the synthesis of new carbon materials with high conductivity and suitable porosity structure to work as a matrix for selenium was well defined and optimized. The microporous carbon (MPC) was synthesized from polyvinylidene fluoride (PVDF) and used as a selenium host for high-performance lithium-selenium (Li-Se) batteries. The microporous carbon/selenium (MPC/Se) composites were optimized in terms of carbonization temperature, and Se/C composite was studied on loaded selenium content and selenium loading on the electrode.

Chapter 5: This chapter is the following work done after optimizing microporous carbon, which has been done in chapter 4. The MPC-800/Se 50 showed the best electrochemical performance in Li-Se batteries, and the optimized composite was employed in Na-Se batteries. The interfacial properties of the Na-Se batteries were then elevated by using the optimized electrode having a sufficient amount of fluoroethylene carbonate (FEC) as the additive in the electrolyte.

Chapter 6: In this chapter, another interfacial cathode surface modification was employed to enhance the Na-Se battery system's electrochemical properties developed in chapter 5. Atomic layer deposition (ALD) was used to protect a microporous carbon/Se (MPC/Se) cathode and reduce polyselenide dissolution, using the optimized electrolyte composition derived from chapter 5 results. The previous coating agent (Alucone) could not completely suppress the polyselenide dissolution into the electrolyte, causing the capacity to decay over long cycles. In this chapter, the coating agent of Al_2O_3 was chosen to improve the electrode's capacity performance and removes the interfacial issues at the electrode-electrolyte interface.

Chapter 7: This chapter summarizes the results derived from all of the works done in this thesis and mainly discusses the suggestions to continue work in this field of study.

Chapter 2: Research methodology

The methodology consists of different preparation steps in regards to reaching the final battery system. This can be various from a carbon source, composite combination, electrolyte and solvents which has been used, *etc*. Therefore, the overall preparation has been described in this chapter, and in the results and discussion section, each battery system assembly feature has been explained in detail.



Methodology

Figure 12. Diagram of the methodology used for the preparation and analysis of the samples.

2.1 Materials synthesis

2.1.1 Synthesis of microporous carbon derived ZIF

ZIF-8 will be synthesized using a recipe including an aqueous solution [106-108]. In a typical process, 1.188 g of Zn (NO₃)₂·6H₂O will be dissolved in 6 mL of DI water (solution A), and 0.656 g of 2-methylimidazole will be dissolved in 7.52 g of an ammonium hydroxide solution (solution B). Solution A will be added to solution B while mixing. ZIF-8 crystallites were collected by centrifugation at 4000 rpm for 10 min. To wash the synthesized ZIF-8, it will

be dispersed in 60 mL DI water and then centrifuged. The washing process will be repeated three times. The final product will be dried in an oven at 60 °C overnight [109]. Microporous carbon will be fabricated by pyrolysis of ZIF-8 at high temperatures (800 °C) under a nitrogen environment. The pyrolysis will be carried out in a chemical vapour deposition system and will yield black powders in the reaction chamber. The black powders are microporous carbon and will be used for the subsequent carbon/selenium composite preparation step.

2.1.2 Synthesis of microporous carbon derived PVDF

Poly (vinylidene fluoride) (PVDF, (-CH₂CF₂-)_n, MW: 64.035 g mol⁻¹, Alfa Aesar) was used as the starting material without further purification. Microporous carbon (MPC) was obtained by direct pyrolysis of PVDF at high temperatures (600, 700, and 800 °C) for 1h under a nitrogen (99.999%) environment. The pyrolysis was performed in a tube furnace (Lindberg/Blue M Mini-Mite) with a heating rate of 10 °C min⁻¹. Black products collected after pyrolysis were MPC, and no further activation on MPC was required. It should be noted that since decomposition of PVDF released corrosive hydrogen fluoride (HF) gas, stainless steel tube was used to hold PVDF, and calcium carbonate aqueous solution was used to neutralize exhausted gas from the tube furnace. From this point forward, the MPC pyrolyzed at 600, 700, and 800 °C was denoted as MPC-600, MPC-700, and MPC-800, respectively.

2.1.3 Synthesis of carbon/selenium composite

Microporous carbon/selenium composites were prepared by a melting diffusion method. [55] Selenium and MPC were mixed in a planetary ball mill for 1h. Then the mixture was transferred and sealed in a stainless steel autoclave under an argon environment (99.999%). The mixture was heated at 260 °C for 12 h, leading to selenium diffusion into carbon pores to obtain MPC/Se.



Figure 13. Tube furnace (Lindberg/Blue M Mini-MiteTM) (left) and stainless steel autoclave (right)

2.2 Structural characterization

Since batteries have found use in new markets, gaining insight into material problems is imperative. The commercialization of new battery technologies demands a suite of mechanical, electrical, and environmental stress testing. Moreover, gaining insight into the materials employed and their behaviour throughout the battery system's life cycle can provide valuable data about the processes taking place within the battery systems and their potential failure mechanisms. Modern batteries consist of various organic, inorganic, and metallic components, with sizes in the range of between Å and cm. It is essential to use the appropriate tools to analyze these components.

2.2.1 Scanning electron microscopy (SEM)

The battery production cycle is a long process that involves several stages. Intermediate checks are necessary to verify the production system's quality, starting from the inspection of raw materials, the production of intermediate components, and reviews on the final product, requiring the method used for the investigations to be highly versatile. Gaining insight into the materials employed in cell production is essential to better understand the parameters that impact a battery's cycle life. Microscopy approaches such as SEM are ideal techniques to analyze particle size, morphology, and particle agglomeration and shortcomings during materials acceptance, process development, and actual production. SEM allows you to improve battery

research by enabling you to magnify your sample hundreds of thousands of times, making features of a few nanometers visible. In this way, it is possible to measure the cross-section of layers and the minor parts' size on the electrode's surface that improve the contact surface. Besides, it is possible to apply both thermal and mechanical stress to a membrane and observe its behaviour on a microscopic level, thus allowing battery researchers to understand the cause of an eventual rupture. Energy-dispersive X-ray microanalysis is often combined with SEM to identify the chemical composition of the sample locally accurately. With an outstanding sub-micron spatial resolution, the analysis only takes a few seconds (Figure 14).



Figure 14. Scanning electron microscope

2.2.2 Transmission electron microscopy (TEM)

The electrochemical performances of batteries are fundamentally determined by the structure and properties of the electrodes and electrolytes. Various characterization techniques have been used to elucidate their process-structure-property relationships to elucidate the material growth, reaction, and capacity fading mechanisms of the electrodes and electrolytes. As an indispensable microscopic tool in materials science, electron microscopy can further extend the understanding of batteries to atomic-level resolution using TEM mode. TEM can generate a wide range of signals carrying structural and chemical information from the real space, reciprocal space, and energy space from the local region of interest in the specimen. Such

information can be presented as high-magnification images, diffraction patterns, and various spectra, respectively. TEM is an effective technique for directly imaging the electrode's microstructural characteristics and solid-electrolyte materials of batteries. The morphology of nanostructured materials, the distribution of multiple phases, and even the atomic arrangements around structurally defective regions can be distinguished from a TEM image. High-resolution TEM (HRTEM) is one of the widely used imaging techniques in TEM mode. HRTEM images usually contain a periodic fringe contrast resulting from the phase interference between the diffracted beams and other transmitted beams, which has resulted in HRTEM becoming a usual coherent imaging method. Because of the phase-contrast phenomenon, HRTEM is sensitive to the defocus value, the specimen thickness, and atoms' distribution. Currently, high-resolution observations of the crystal and electronic structure of the electrode and electrolyte materials in real space are convenient with the TEM technique. TEM is usually required to provide phase maps of the electrode or electrolyte materials, and the dark-field imaging technique is generally a conventional solution to this task.

2.2.3 X-ray diffraction (XRD)

X-ray diffraction is a characterization technique that reveals the crystallographic structure, lattice parameters, planar spacing, crystallite size, *etc*. This technique works on the principle of Bragg's law, where the material is bombarded with X-rays at different angles, and the intensity of the beam is measured. If sharp peaks are observed, these peaks are used for analyzing the structure of the material, lattice parameters and for determining the formation of a pure phase and most importantly, it is used to identify the presence of any unknown substances by comparing the observed diffraction data against a database maintained by the International Centre for Diffraction Data. The XRD is a low-cost and highly technical technique because of

this technique's simple physical principles. One of XRD's benefits is the lack of vacuum, which reduces construction costs and places it at a higher level than electronic techniques. Besides, the XRD is a non-contact and non-destructive technique and does not require complex preparation.

2.2.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is an analytical technique that measures the valence states, elemental composition, and the empirical formula of the elements that are present within a material. XPS spectra are obtained by bombarding a fabric with a beam of X-rays while simultaneously measuring the kinetic energy and the number of electrons that escape from the material. A by-product of the charge and discharge process is forming the solid-electrolyte interphase layer on the anode/cathode. The formation and development of the SEI layer effects battery performance. Understanding the SEI layer is an area of significant interest to be controlled and therefore improve cell performance. XPS depth profiling offers a way of chemically characterizing the complex mix that makes up the interphase layer, allowing identification of the chemistries that comprise the SEI (Figure 15).



Figure 15. Schematic diagram of X-ray photoelectron spectroscopy [110]

2.2.5 Brunauer-Emmett-Teller specific surface area (BET)

To facilitate lithium-ion transport between the electrodes using the electrolyte within the 54

cell, electrode materials need to be porous. Control of the porosity increases the interactions between the electrode and the conductive diluents and increases the intra-electrode conductivity with adequate lithium-ion intercalation. A high surface area reduces the diffusion distance within electrodes and facilitates ion exchange between the electrode and the electrolyte, improving the efficiency of the electrochemical reactions. However, there can be some associated problems with a higher surface area due to the electrode being more degraded through increased electrolyte reactions, and in turn, causing the electrode to exhibit a lower thermal stability and capacity loss. The optimization of the electrode materials' surface area is essential for providing the ideal balance of properties. BET surface area measurements for electrode materials using nitrogen gas physisorption have made this possible. The size and shape of the pores in the electrody material significantly affect the transport properties of the lithium ions through the electrolyte, with a direct influence on the energy density, power, lifetime, and reliability of batteries. Understanding how the pores connect with other adjacent pores, closed pores, and channels within the electrode material help ensure that an optimal electrolyte and electrode interaction is achieved.

2.3 Electrochemical characterization

The cycling performance of the coin cells was tested in different voltage ranges on a Neware BTS 4000 battery testing system. After the battery test, we can obtain information about capacity, cycling performance, rate performance, and coulombic efficiency. A battery's ability is the product of the total amount of charge when completely discharged under given conditions and time. Battery capacity can be measured using gravimetric specific capacity (mAh g⁻¹, mAh g⁻¹) or volumetric specific capacity (Ah I⁻¹, mAh cm³). Cycle life is the number of charge and discharge cycles that a battery can achieve before its capacity is depleted. A high-performance battery should be able to maintain its capacity even after numerous charge and discharge cycles. The cycle life of lithium secondary batteries strongly depends on electrode active materials'

structural stability during the charging/discharging process. Irreversible capacity, which is the amount of charge lost, is usually observed after the first charge/discharge cycle and results from forming a new layer at the interface of electrodes and electrolytes. Coulombic efficiency is the ratio of the output of charge by a battery to the input of charge. The internal resistance of a cell determines Coulombic efficiency. Rated Capacity is the number of ampere-hours a battery can deliver under specific (rate of discharge, end voltage, temperature) conditions. Usually, researchers will test batteries' capacity in higher current density to measure batteries' fast charge ability.

Cyclic voltammetry testing was performed on a biologic VSP potentiostat/galvanostat station in the voltage range of 1–3/0.5-3.5 V at a scan rate of 0.2 mV s⁻¹. Cyclic voltammetry is an electrochemical analysis method that scans voltage with a constant voltage scan rate for a given potential range of an electrochemical cell. Cyclic voltammetry observes changes in current by applying voltage under a constant scan rate. It repeats the same experiment for each cycle. Current-voltage curves obtained from cyclic voltammetry provide information on redox reactions occurring within the cell, including (1) potential, (2) quantity of electricity, (3) reversibility, and (4) continuity (sustainability of reversible electrochemical reaction). While the scan rate differs depending on the experiments' purpose, a low scan rate is recommended for detailed electrochemical reactions. Electrochemical Impedance Spectroscopy (EIS) test is an electrochemical method used to examine current response under AC voltage to obtain resistance, capacitance, and inductance values. In an EIS test, we can acquire information such as batteries' inner resistance. The electrical chemical test for the battery was taken by an electrochemical workstation (Biologic VSP Potentiostat/ Galvanostat Station).



Figure 16. 80-Channel battery tester- VSP potentiostat

2.3.1 Electrode fabrication

To prepare the cathode electrode, 80 wt% of MPC/Se composite, 10 wt% of carbon black, and 10 wt% of sodium alginate (in 0.5 wt% aqueous solutions) were mixed thoroughly to form a uniform slurry. The slurry was then pasted on an aluminum foil using a doctor blade. The electrode was dried entirely at 50 °C under vacuum overnight. After that, the electrode was cut into round disks with diameters of 0.5 inches.



Figure 17. Vacuum oven (left) - Battery disc cutter (right)

2.3.2 Atomic layer deposition

Atomic layer deposition (ALD) has attracted increasing attention in recent years, and they

have great potential when applying in next-generation LIBs [111]. ALD is a thin film deposition technique that is an essential feature: saturating and irreversible, also called self-limiting and self-terminating. In an ALD process, each precursor was exposed to the substrate surface. Only a certain amount of material was adsorbed on the substrate, no matter how much reactant was available. This automatic control of the amount of material deposited is the key characteristic of ALD. Due to the unique reaction mechanism of ALD, this advanced deposition method has lots of advantages. ALD can fabricate a uniform thickness controllable thin film on a complex surface, for example, on a three-dimensional (3D) substrates [112]. Furthermore, the ALD process has weak temperature dependency. (It can be applied even down to room temperature (RT)) [112, 113]. Unlike the CVD process, which is strongly temperature-dependent due to the Arrhenius-type film growth mechanism, the amount deposited by ALD per cycle depends on the conditions where the reactions are carried out (reactants, substrate).



Figure 18. The digital picture of the complete view of the atomic layer deposition equipment.

2.3.3 Battery assembly

Coin cells were assembled in an argon (99.999%) filled glovebox with H₂O and O₂ levels

below 0.1 ppm. The cell consisted of the prepared Se/C as a cathode, Li or Na metal as the anode, Celgard 2500 or glass fibre as a separator, and 1 M LiPF₆ or 1M NaClO₄ in ethylene carbonate, diethyl carbonate with/without fluoroethylene carbonate as the electrolyte. Firstly, the dried electrode was cut into 2 cm² circular discs. The counter electrode was lithium/sodium metal foil in a half battery. Then we can choose different electrolytes and additives based on our experiment. Finally, we put the electrodes, electrolyte, separator, and supporting part of the battery in the coin cell and assemble them by a crimping machine.



Figure 19. Glovebox workstation

Chapter 3: Synthesis of Microporous Carbon from Metal-Organic Framework as a Matrix for Selenium in Lithium-Selenium Batteries^{*}

The first chapter of results mainly discusses the first carbon synthesis approach employed as a selenium host in Li/Na batteries. We use our chemistry and materials science expertise to develop high-performance Li/Se batteries for EV applications by materials innovation. To do so, preparation of carbon host is a must, which needs to be focused on different parameters such as the correlation between materials structure (especially pore size and volume) and battery performance, and provide guidelines for battery cathode design next steps. This chapter developed a novel microporous carbon/Se cathode by using zeolitic imidazolate framework-8 (ZIF-8), a subclass of MOFs, as the microporous carbon source to build a Li-Se battery and make the advancement of fundamental knowledge in materials surface/interface science. Carbon from MOF is expected to exhibit high porosity, conductivity, and surface area with chemical stability. By investigating the carbon produced in this chapter and the electrochemical data derived from the Li-Se batteries made with the C/Se composite, the suitable electrode for this battery system would be more apparent. If the carbon could satisfy the capacity performance needed to compete with the current development in the Li-Se batteries, the rest of the work can be done on this carbon type. Otherwise, this chapter's results can be a guideline to synthesize and optimize a carbon matrix as a host for selenium in Li-Se batteries. This is the first step of the current study in which the composite/electrode should be modified, and then the interface design will help the elaborated electrode architecture.

^{*} CRediT authorship contribution statement

Mohammad Hossein Aboonasr Shiraz: Conceptualization, Investigation, Writing - original draft. Hossein Kazemian: Methodology, Formal analysis, Writing - review & editing, Funding acquisition. Jian Liu: Supervision

The rising level of greenhouse gases caused by the increased use of fossil fuels is one of the foremost drivers of climate change. In Canada, the transportation sector was the second-largest source of greenhouse gases, accounting for 23% of total emissions in 2014 [114]. This greenhouse gas pollution has contributed to global climate change and presented a significant threat to Canadians' health and the environment upon which our economy and security depend. Electric vehicles (EVs) are gaining worldwide popularity as cleaner alternatives to internal combustion engine vehicles. EVs, such as Tesla Model S, Nissan Leaf, use electric motors as the power and lithium-ion batteries to store and supply electricity to the motors. They produce low or zero greenhouse gases and represent the future of cars. However, current EVs still have a limited driving range, and drivers fear that their vehicles have insufficient capacity to reach their destinations (so-called "range anxiety"). The main reason is rooted in lithium-ion batteries used in EVs [115, 116]. The storage capacity of vehicular lithium-ion batteries with higher storage capacities (400-500Wh/kg).

Lithium-sulfur (Li-S) and lithium-selenium (Li-Se) batteries have attracted considerable attention as alternatives to lithium-ion batteries for EV applications. Li-S batteries provide a high theoretical energy density (1672 mAh g⁻¹) but face a critical challenge in achieving areal capacities for practical application due to the poor electronic conductivity of S (5×10^{-28} S m⁻¹) [117]. On the other hand, Li-Se batteries have the advantage of high electronic conductivity of S (1×10^{-3} S m⁻¹) but suffer from much lower energy density (675 mAh g⁻¹) [118].

The use of microporous carbon as a cathode (S or Se) host has been demonstrated as a practical approach to increase Li-S and Li-Se batteries' performance. Therefore, it is reasonable to believe that impregnation of Se into tiny pores (1-3 nm) of carbon could increase the

electronic conductivity, reduce diffusion length of lithium ions, and enhance the electrochemical properties of Li-Se batteries. Among different ways of preparing microporous carbon, pyrolysis of metal-organic frameworks (MOFs) is a promising one. MOFs have three-dimensional structures consisting of metal ions that are linked by organic ligands and have emerged as a novel type of crystalline porous materials, which combine highly desirable properties such as microporosity, high surface area, and exceptional thermal and chemical stability [119]. Pyrolysis of MOFs could yield microporous carbon with tunable pore size, controlled pore distribution, and extremely high surface area, which is essential to obtaining high performance in Li-Se batteries.

3.1 Materials synthesis

3.1.1 Synthesis of ZIF

Zeolitic imidazole framework-8 (ZIF-8) was synthesized using an aqueous solution method. In a typical process, two different solutions were prepared as follows. The first solution consists of 1.188 g of Zn (NO₃)₂·6H₂O dissolved in 6 mL of DI water and mixed at room temperature. The second solution was the mixing of 0.656 g of 2-methylimidazole and 7.52 g of an ammonium hydroxide solution. The first solution was added to the second one under the same condition, forming a milky solution. The product was collected using a centrifuge at 4000 rpm for 10 min. The product was dispersed in 60 mL DI water under vigorous stirring and then collected using a centrifuge to remove the residual materials. The ZIF-8 crystals were dried at 60 °C for 12 h, and the white powder was collected and denoted as "ZIF".

3.1.2 Synthesis of microporous carbon derived ZIF and Se/C composite

Microporous carbon was fabricated by pyrolysis of ZIF-8 in a tube furnace (Lindberg/Blue M Mini-Mite[™]) at the temperature of 800 °C with a heating rate of 10 °C min⁻¹ and kept for 6 h under the protection of argon gas atmosphere (argon 99.999%). The as-formed black powder was 62

washed with 37% hydrochloric acid, deionized water, ethanol, and dried in a vacuum oven at 70 °C for 12 h named "CZIF". The Se/CZIF composite was prepared by the melt diffusion method. For this, sublimed selenium powder, -100 mesh (99.5%, Sigma Aldrich), and CZIF were mixed in a ratio of 1:1 to reach a homogenous powder and then sealed in a 50 mL stainless steel autoclave under the protection of argon gas. The mixture was then heated up to the temperature of 260 °C for 12 h. The melting diffusion method used the capillary force to diffuse Se into microspores of CZIF. Cathode electrodes were prepared by mixing Se/CZIF composite, carbon black (MTI Co.), and sodium alginate (Ward's Science Co., Ltd., 0.5 wt% aqueous solutions) with a ratio of 8:1:1 to form a slurry and then cast on the Al foil current collector by using a doctor blade. The electrode was then vacuum dried at 60 °C overnight and then put into the MLD equipment for coating.

The coating of Alucone on the Se/CZIF electrode was performed at 100 °C by supplying trimethylaluminum (TMA) and glycerol into a commercial MLD reactor (GEMStarTM XT Molecular Layer Deposition Systems, Arradiance, USA). The thickness of Alucone on Se/CZIF cathode was adjusted by using 5, 10, and 20 MLD cycles (each cycle ~ 0.1 nm), and the prepared sample was designated as Se/CZIF- 5 Alucone, Se/CZIF- 10 Alucone, and Se/CZIF- 20 Alucone, respectively. Subsequently, the electrode was cut into round disks with a diameter of 12.7 mm for coin-cell assembly.

3.1.3 Electrochemical characterization of Se/C cathode in Li-Se batteries

Electrochemical testing of Se/CZIF composite was carried out using CR2016 coin cells. Coin cells was assembled in an argon-filled glovebox (H₂O, O₂ < 0.1 ppm) with 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1: 1, v/v) with 3 vol.% FEC (abbreviated as LiPF₆/EC-DEC+FEC), a Celgard 2400 (Celgard, USA) separator, and a pure Li foil (Alfa Aesar, 99.9%) anode. Galvanostatic charge/discharge conducted using a multi-channel battery testing system in the voltage range of 1.0-3.0 V (vs. Li/Li⁺) at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) characterizations were performed to investigate the electrochemical performance of cathodes in lithium-selenium batteries.



3.2 Results and discussion

Figure 20. (a) SEM images, (b) XRD pattern, and (c) TGA Spectrum of synthesized ZIF.

Figure 20a shows the SEM images of the synthesized ZIF. The cubic shapes of ZIF particles can be seen in pictures, corresponding to the crystalline structure of prepared ZIF. To investigate the findings in SEM images, the XRD analysis was performed (Figure 20b) where the samples' exhibit sharp and high-intensity ZIF-8 characteristic peaks at 2θ of 7.3°, 10.3°, 12.8°, 14.4, 16.5°, 22.2° and 24.5° that indicates the formation of highly cubic shape crystalline ZIF-8 products [120]. Figure 21a shows the SEM images of carbon derived from ZIF-8 (CZIF). The morphologies represent the irregular amorphous structure with some cubic-rounded shaped particles. The mean particle size was determined as 0.79 µm.



Figure 21. (a) SEM images of carbon derived from ZIF at different magnifications, (b) XRD patterns of CZIF, Se/CZIF composite, and Se powder, (c) TGA Spectrum of Se/CZIF composite

The XRD patterns of carbonized ZIF-8 show only one broad peak located at about 25°, suggesting the amorphous nature of CZIF. For Se/CZIF composite, sharp diffraction peaks have been seen that could be assigned to pure Se. These Se peaks are located at 23.4°, 29.6°, 41.2°, 43.6°, 45.5°, 51.6°, 56.2°, 61.6°, 65.3° (JCPDS No: 06-0362), respectively. The reason for showing Se peaks in Se/CZIF compare to CZIF could be due to the existence of Se on the surface of carbon derived from ZIF. In Se/CZIF composite, the carbon pores were filled up with selenium. The residue was distributed as a bulk selenium layer on the carbon matrix, contributing to the strong XRD diffraction peaks for Se/CZIF.

Thermogravimetric analysis (TGA) of the ZIF sample has been depicted in Figure 20c. The first weight loss of 5% up to the temperature of 140 °C is related to the release of H₂O and other absorbed un-reacted molecules. No weight loss was seen before reaching the temperature of about 400 °C, confirming the structural stability of the as-synthesized ZIF-8. A sharp weight loss was happened right after due to structural degradation and decomposition of organic ligands. The TGA of Se/CZIF composite (Figure 21c) shows a multi-step weight-loss of about 60% to reach the temperature of 900 °C, demonstrating the removal of selenium from the external and internal part of the carbon pores, respectively.



Figure 22. (a) Cycling performance and (b) Coulombic efficiency of Se/CZIF, Se/CZIF - 5 Alucone, Se/CZIF - 10 Alucone and Se/CZIF - 20 Alucone measured at 0.1 C (1 C=678 mA/g); charge-discharge profiles of Se/CZIF and Se/CZIF - 5 Alucone in the (c) 1st cycle, (d)) 40th cycle, and (e) 75th cycle; (f) rate capability of Se/CZIF and Se/CZIF - 5 Alucone.

The influence of Alucone coating on the electrochemical performance of Se/CZIF cathode is studied in Li-Se batteries between 1V and 3V at 0.1C, and the results are shown in Figure 22. As shown in Figure 22a, Se/CZIF-5 Alucone exhibits an initial discharge capacity of about 820 mAh g⁻¹, while for pristine Se/CZIF, Se/CZIF-10 Alucone, and Se/CZIF-20 Alucone, the specific discharge capacity of 768, 740, and 745 mAh g⁻¹ are delivered, respectively. This indicates the effect of 0.5 nm thickness of the Alucone coating on improving the Se/CZIF composite's capacity performance. After the 1st cycle, the capacity dropped in all of the samples could be ascribed to the formation of SEI film and the decomposition of electrolytes on the MPC/Se cathode [90]. After the first cycle, the Se/CZIF-5 Alucone kept its higher capacity among the other samples over 80 cycles. For Se/CZIF, the capacity decreases gradually from 513 mAh g⁻¹ in the 2nd cycle to 402 mAh g⁻¹ after 80 cycles. In contrast, Se/CZIF-5 Alucone coating could still deliver a specific capacity of 466 mAh g⁻¹ after 80 cycles. Moreover, after 80 cycles, Se/CZIF-20 Alucone exhibits a specific capacity lower than Se/CZIF-5 Alucone and Se/CZIF-10 Alucone but better than the new Se/CZIF cathode. This shows the effect of Alucone coating on both elevating and stability of the electrochemical properties of Se/CZIF composite. Further increase of Alucone coating for more than 5 cycles (~ 0.5 nm) causes a noticeable decrease in the specific capacity. The reason could be due to the insulating nature of Alucone coating, which might slow down the diffusion of Li ions through the SEI layer [121-124]. This result suggests the importance of Alucone coating thickness for achieving optimal protection effect in Se cathodes. Except for the first cycle, coulombic efficiency is close to 100% for Se/CZIF-5 Alucone, implying that Alucone coating reduces the side reaction between the electrode and the electrolyte (Figure 22b).

Figure 22c-22e presents charge/discharge curves of the Se/CZIF and Se/CZIF-5 Alucone in

the 1st, 40th, and 75th cycle tested at 0.1C. As shown in Figure 22c, both Se/CZIF and Se/CZIF - 5 Alucone exhibit one prominent plateau during the discharge and charge process, characteristic of micropore-confined Se [90, 125-128]. Moreover, it is found from Figures 22d and 22e that Alucone coating also minimizes the polarization of the Se/CZIF cathode during the discharge and charge process. This indicates the enhancement in reaction kinetics of Se/CZIF by Alucone coating. The improved capacity and kinetics in Se/CZIF- 5 Alucone could result from the protective effect of nanoscale Alucone coating, which alleviates polyselenide dissolution and reduces solid deposit deposits polyselenides. Better rate capability was also seen in Se/CZIF-5 Alucone, a benefit of better kinetic (Figure 22f).



Figure 23. (a, b) CV curves of Se/CZIF and Se/CZIF - 5 Alucone in different cycles.

To find out the reasons for the improved performance by Alucone coating, CV analysis was performed on the Se/CZIF and Se/CZIF- 5 Alucone cathodes at a scan rate of 0.2 mV s⁻¹, and the results in the first five cycles are shown in Figure 23a-b. What is clear from the first sight of the CV curves comparison is that for the Se/CZIF-5 Alucone cathode, the oxidation and reduction peaks have a relatively better overlapping, indicating the enhanced reversibility of the Se/CZIF cathode by Alucone coating. Additionally, the separation between oxidation and reduction peaks of Se/CZIF cathode is reduced from 0.8V to 0.5V in the 5th cycle with Alucone

coating, indicating better kinetics in Se/CZIF-5 Alucone cathode. For Se/CZIF cathode, the reduction peaks show a shoulder in all cycles, suggesting a multi-step phase transformation from Se to Li₂Se. An apparent decrease in the shoulder intensity has been seen in Se/CZIF-5 Alucone, offering a better kinetic and suppression of polyselenide dissolution with Alucone coating. The comparison between Figure 23a and 23b suggests that the Alucone coating effectively suppresses the dissolution of polyselenides from Se/CZIF cathode into the carbonate electrolyte, a stable protecting layer of the Se/CZIF cathode via the ALD technique. In particular, this rigid coating layer on the cathode surface was crucial for alloying- and conversion-type electrodes, which accompanied dramatic volume changes upon the lithiation-delithiation process.

This chapter mainly investigates the carbon source derived from the metal-organic framework as a host for selenium to be employed in Li/Na-Se batteries. This chapter's result can lead to the following works in terms of carbon source, selenium loading, and the electrochemical properties expected from the cathode. The simplicity for the synthesis of the ZIF and carbon derived from that is one of the advantages of this work. Besides, some other preparation methods for ZIF are based on using organic solvents such as methanol/DMF, while in this work, the water-based solution was used. Typically the carbons are needed to be activated by using the KOH activation technique to make more pores in the carbon structure. The benefit of the asprepared carbon derived from ZIF is its activation-free nature, which can confine selenium up to the content of about 40%.

On the contrary, the selenium loading in this carbon source was not sufficient to be considered a promising candidate for this battery system cathode. Therefore, finding an alternative carbon matrix is necessary to satisfy the energy demand. The electrochemical properties of the prepared cathode were good but not stable enough. The capacity of the SE/CZIF cathode could be elevated by using the Alucone coating. However, it fades gradually over cycles.

The results mentioned above indicated that the carbon matrix's progress is necessary to improve the targeted batteries' efficiency. Besides, the electrode/electrolyte interface needs some improvements regarding the suppression of polyselenide dissolution into the electrolyte. The Alucone coating needs to be replaced with a better protecting layer to improve the cathode structure stability (cathode side). In contrast, on the other side of the electrode/electrolyte interface, the electrolyte should play a significant role in prohibiting the polyselenide penetration into the electrolyte. Our following goals are based on trying these objectives to find the solutions for them.

Chapter 4: Activation-Free Synthesis of Microporous Carbon from Polyvinylidene Fluoride as Host Materials for Lithium-Selenium Batteries[†]

This chapter is the next stage of the previous chapter, in which the carbon derived from ZIF-8 showed relatively stable capacity performance over cycles. However, to compete with recent advances in Li-Se batteries done so far, it could not fully meet the minimum requirements of electrochemical performances expected from a host to confine selenium. The Se/CZIF could not retain the rate capability during charge/discharge, and the capacity faded over the cycle lifetime. The issues mentioned above move the work towards the synthesis of new carbon materials with high conductivity and suitable porosity structure to work as a matrix for selenium in MPC/Se composite. The method to prepare the carbon should be facile enough to be used in practical applications while maintaining the characteristics needed for selenium to diffuse in. Therefore, microporous carbon (MPC) was synthesized from polyvinylidene fluoride (PVDF) using an activation-free approach and used as a selenium host for high-performance lithiumselenium (Li-Se) batteries. The microporous carbon/selenium (MPC/Se) composites were applied as a cathode in Li-Se batteries with a carbonate-based electrolyte. The influences of PVDF carbonization temperature (600 °C, 700 °C, and 800 °C) and Se content (50 wt%, 60 wt%, and 70 wt%) in the cathode were investigated to establish a correlation between MPC structure and MPC/Se electrochemical performance. The results revealed that the MPC/Se composite cathode, with MPC synthesized at 800 °C and a Se content of 50 wt%, exhibited a superior

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reversible capacity of 508.8 mAh g⁻¹ at 0.1C after 100 cycles.

Moreover, the MPC/Se maintained a capacity retention of 354.0 mAh g⁻¹ at 0.5 C for 200 cycles. The excellent performance could be attributed to the dominant microporous feature of MPC, which could effectively confine Se and reduce side reactions with electrolytes. Furthermore, increasing Se content from 50 wt% to 70 wt% led to a decrease in the specific capacity and rate capability of MPC/Se cathode due to significantly reduced Li-ion diffusion coefficient. This work suggested the effectiveness of MPC derived from commercial PVDF through an activation-free and scalable approach as Se hosts for high-performance Li-Se batteries.

Nowadays, energy storage is one of the top-rated concerns to increase the deployment of renewable energy globally, decrease the dependence on fossil fuels, and reduce greenhouse gas emissions. Lithium-ion batteries are the most popularly used energy storage technology for many applications, such as electric vehicles, portable devices, and grid storage, due to their relatively high energy density and low cost [129]. However, the end-users fast-growing demands call for battery technologies with higher capacity, longer lifetime, and lower price. Lithium-ion batteries are reaching the bottleneck of their performance due to the battery chemistry limitation and cannot satisfy these increasing requirements [115, 130]. Recently, lithium-sulphur (Li–S) batteries have drawn significant attention owing to their high theoretical energy density of 2570 Wh kg⁻¹ and the low cost of S [117, 131]. Despite considerable progress made over the past years, Li-S batteries still face many challenges associated with the insulating nature of S and "shuttle effect" phenomena, which results from the dissolution of high-order polysulfide intermediates in ether-based electrolytes. It is urgent to develop alternatives to the S cathode to enable high-performance lithium-based batteries.
Recently, elemental selenium (Se) has attracted increasing attention as a promising cathode material to build lithium-selenium (Li-Se) batteries. Se is a *d*-electron-containing member in the same elemental group as S in the periodic table and has a considerably higher electronic conductivity of 1×10^{-3} S m⁻¹ than S (5×10^{-28} S m⁻¹) [17, 73, 95]. The reaction of Se with Li follows 2Li^+ + Se + 2e⁻ \leftrightarrow Li₂Se, corresponding to a gravimetric capacity of 675 mAh g⁻¹, which is much lower than that of S (1672 mAh g⁻¹). However, Se possesses a high density of 4.2 g cm⁻³ and provides a high theoretical volumetric capacity of 3253 mAh cm⁻³, comparable to S (3467 mAh cm⁻³) [95]. Since Amine and co-authors' first report in 2012 [73], these advantages of Se in electronic conductivity and volumetric energy density have motivated researchers to explore the possibility of using Se as a cathode for Li-Se batteries.

Earlier work employed bulk Se or nanostructured Se cathodes for ether-based electrolytes in Li-Se batteries [60, 62, 132]. Like S cathodes, Se cathodes exhibited severe shuttle effect, limited life cycle, and Coulombic efficiency in ether-based electrolytes due to highly reactive high-order polyselenides (Li₂Se_x, x>4). Later on, it was reported that polyselenides were insoluble in carbonate-based electrolytes [133]. As a result, Se cathode, especially spaceconfined Se, were more compatible with carbonate-based electrolytes and showed high capacity and outstanding cycling stability [84-86, 88-90, 134-136]. In carbonate-based electrolytes, Se undergoes a one-step reaction from Se to Li₂Se, without the formation of unstable polyselenide intermediates, and is featured with one single plateau in its charge-discharge curves [17, 95]. Therefore, Li-Se batteries' development based on carbonate-based electrolytes represents a promising approach to developing alternatives to LIBs and Li-S batteries.

The rational design of the Se cathode is the key to enabling high-capacity and durable Li-Se batteries. In particular, confining Se in a porous carbon matrix has been proven as an effective approach to enable high-performance Se cathode for Li-Se batteries. In recent work, various porous carbon materials have been developed as Se hosts to improve the overall performance of Li-Se batteries, including hierarchical porous carbon derived from the metal-organic framework (MOF) or zeolitic imidazolate framework (ZIF) [84, 86, 134], nitrogen-doped microporous carbon [85, 135], and porous carbon spheres [88-90, 136]. For instance, Guo et al. prepared an ordered mesoporous carbon (CMK-3) matrix as a Se host and demonstrated a high discharge capacity of 670 mAh g⁻¹ at 0.1C for the Se/CMK-3 cathode [136]. In another work, by using ZIF-derived microporous carbon and novel electrolyte additives (LiDFOB and FEC), Wang et al. achieved a capacity of 511 mAh g⁻¹ for 1,000 cycles at 5C, with a capacity decay of 0.012% per cycle for the nanostructured Se cathode [134]. Despite this great progress in Se cathode design, the synthesis of porous carbon materials used in these works involved complex processes and expensive precursors (as summarized in Table 4), making them difficult to scale up for practical applications. For example, although ZIF-8 derived carbon nanoparticles (~ 35 nm) promised fast kinetics and good rate capability for Se cathode, the preparation of these carbon nanoparticles consisted of several steps, *i.e.*, synthesis of ZIF-8, followed by carbonization at high temperatures and then washing with an HCl solution [86, 134]. In another two studies, polyacrylonitrile nanofibers [82] and polypyrrole spheres [85] were first synthesized, then carbonized, and finally chemically activated using KOH, followed by a washing process. Furthermore, the majority of Se cathodes reported so far have relatively low Se loading (< 1 mg cm⁻²) and Se content (< 50 wt%) [84-86, 88-90, 134-137]. Se loading represents the mass of Se per unit electrode area, while Se content stands for the weight percentage of Se in the Se/C composites. Ideally, both Se loading and Se content should reach as high as possible to achieve high energy density in Li-Se batteries at the battery system level [138, 139]. To address the limitations mentioned above, therefore, it is imperative to develop an easy, scalable, and lowcost fabrication approach for porous carbon material with preferably high Se loading and Se content in Se/C cathode composites for Li-Se batteries.

Herein, we developed a one-step activation-free process to fabricate microporous carbon (MPC) as Se hosts for Li-Se batteries based on a carbonate electrolyte. This work has three highlights as follows. First of all, MPC with a high surface area (830.0 m² g⁻¹) and micropores (1-3 nm) dominant structure were prepared by direct pyrolysis of commercial polyvinylidene fluoride (PVDF) powders in one step and used for Se infiltration without any further activation. The MPC synthesis method is easy to scale up at a relatively low cost. Secondly, the optimal MPC/Se composite cathode showed a high reversible specific capacity of 530 mAh g⁻¹ and high Coulombic efficiency (CE) over 99.5% at 0.1C. It maintained a capacity of 400 mAh g⁻¹ at 0.5C for 200 cycles with a high Se loading of 1.4 mg cm⁻². Finally, yet importantly, this work established the correlations between the physical properties of MPC, Se loadings and Se contents, and electrochemical properties of MPC/Se cathode and pinpointed the key factors governing the performance of Li-Se batteries in carbonate-based electrolytes.

4.1.1 Preparation of MPC and MPC/Se composites

Poly (vinylidene fluoride) (PVDF, (-CH₂CF₂-)_n, MW: 64.035 g mol⁻¹, Alfa Aesar) was used as the starting material without further purification. Microporous carbon (MPC) was obtained by direct pyrolysis of PVDF at high temperatures (600, 700 and 800 °C) for 1h under a nitrogen (99.999%) environment. The pyrolysis was performed in a tube furnace (Lindberg/Blue M Mini-Mite) with a heating rate of 10 °C min⁻¹. Black products collected after pyrolysis were MPC, and no further activation on MPC was required. It should be noted that since decomposition of PVDF released corrosive hydrogen fluoride (HF) gas, stainless steel tube was used to hold PVDF and calcium carbonate aqueous solution was used to neutralize exhausted gas from the tube furnace. From this point forward, the MPC pyrolyzed at 600, 700 and 800 °C was denoted as MPC-600, MPC-700 and MPC-800, respectively.

MPC and Se composites (MPC/Se) were prepared by a melting diffusion method. Briefly, MPC and Se powders (99.5%, Sigma Aldrich) were firstly mixed in different weight ratios (50:50, 40:60, and 30:70) in a mortar for 1h. Secondly, the MPC and Se mixture was sealed in a 50 mL stainless-steel autoclave under an argon (99.999%) environment. Lastly, the autoclave was heated to 260 °C and hold for 12 h to facilitate the diffusion of Se into MPC microspores due to capillary forces. The obtained MPC/Se composites with nominal Se loadings of 50 wt%, 60 wt%, and 70 wt% were designated as MPC-X/Se 50, MPC-X/Se 60, and MPC-X/Se 70, respectively, where X equals 600, 700 and 800 (carbonization temperatures). The actual Se loadings in the MPC/Se composites were measured by thermogravimetric (TG) analysis (TGA, NETZSCH STA 449F3).

4.1.2 Electrochemical characterizations of MPC/Se composites

The electrochemical properties of the MPC/Se composites were evaluated in CR 2032 coin cells by using Li foil as the counter electrode. To prepare the cathode electrode, 80 wt% of MPC/Se composite, 10 wt% of carbon black (MTI), and 10 wt% of sodium alginate (Ward's Science Co., Ltd., 0.5 wt% aqueous solutions) were mixed thoroughly to form a uniform slurry. The slurry was then pasted on an aluminum foil using a doctor blade. The electrode was completely dried at 50 °C under vacuum overnight. After that, the electrode was cut into round disks with a diameter of 12.7 mm and Se loadings in a range of 1.4 to 2.0 mg cm⁻². Coin cells were assembled in argon (99.999%) filled glovebox workstation with H₂O and O₂ level below 0.1 ppm. One coin cell consisted of one Se/C electrode as the cathode, one Li metal as the anode,

Celgard 2500 as the separator. The electrolyte used is 1 M LiPF₆ in ethylene carbonate:diethyl carbonate (EC:DEC, 1:1 volume ratio). The cycling performance of the coin cells was tested in the voltage range of 1 - 3 V (or 0.5 - 3V) on a Neware BTS 4000 battery testing system. Cyclic voltammetry (CV) testing was performed on a Biologic VSP Potentiostat/ Galvanostat Station in the voltage range of 1-3V (*vs.* Li⁺/Li) at a scan rate of 0.2 mV s⁻¹. The electrochemical testing was conducted at room temperature of 25 °C.

4.2 **Results and Discussion**



Figure 24. Schematic illustration of the preparation process for microporous carbon (MPC) by the direct carbonization of PVDF at 600 – 800 °C for 1h in N₂ atmosphere (Step 1), and for MPC/Se composites by melting diffusion of Se powders into MPC at 260 °C for 12h (Step 2).

Figure 24 illustrates the preparation process for microporous carbon (MPC) and MPC/Se composites. The MPC is synthesized from one-step carbonization of PVDF at temperatures of 600-800°C in an N₂ environment for 1h. In the first step, thermal decomposition of PVDF leads to the formation of micropores in MPC structure and is accompanied by corrosive HF gas release [140-142]. In the second step, MPC was mixed with Se powders in various weight ratios (50:50, 40:60, and 30:70), and the mixture was annealed at 260 °C for 12h to infiltrate Se into the pores of MPC to form MPC/Se composites.



Figure 25. (a) SEM image, (b) HRTEM image, and (c) BET isotherms and pore size distribution (inset) of MPC-800; (d) SEM image, (e) STEM image and EDS elemental mapping of C and Se, and (f) XRD patterns of MPC-800/Se 50, in comparison with MPC-800 and Se powders.



Figure 26. EDS spectrum of MPC-800/Se 50 under STEM mode. Cu is from the Cu mesh support grid for HRTEM.

Figure 25 shows the morphology and structure of MPC and MPC/Se composites. The obtained MPC possesses irregular shapes with particle sizes of about 10-100 µm, as seen in Figure 25a. High-resolution transmission electron microscopy (HRTEM) observation discloses the presence of short-range ordered carbon layers and many micropores less than 3 nm embedded in MPC structure, as pointed by the white arrows in Figure 25b. Figure 25c presents BET isotherms, and pore size distribution of MPC carbonized at 800°C (MPC-800). MPC-800

exhibits type I isotherm with the significant feature of "microporous solids" [140, 141]. The knee of adsorption took place at very low pressure, and the plateau is relatively flat, indicating a strong interaction between pore walls and adsorbate, as a feature of highly microporous carbon [140, 141]. The insert in Figure 25c shows the pore size distribution of MPC-800, which exhibits a narrow single modal pore size distribution between 1-3 nm in the micropore region. MPC-700 and MPC-600 possess similar features in BET isotherms, as will be discussed later on. Compared to MPC, MPC/Se composites show no noticeable morphology change (Figure 25d). EDS elemental mapping under Scanning Transmission Electron Microscopy (STEM) mode confirms C and Se's existence (Figure 26) and the uniform distribution of Se in MPC carbon structure, as seen in Figure 25e. X-ray diffraction (XRD) patterns of pristine Se, MPC-800, and MPC-800 with a Se content of 50% (MPC-800/Se 50) are shown in Figure 25f. It can be seen that pure Se powders exhibit sharp and intense peaks. Diffraction peaks of pure Se are located at 23.5°, 29.7°, 41.3°, 43.7°, 45.4°, 51.7°, 56.1°, 61.7°, 65.2°, corresponding to (100), (101), (110), (012), (111), (201), (112), (022), (120) planes of trigonal Se (JCPDS No: 06-0362), respectively. For MPC-800, only one broad peak is detected in its XRD pattern, suggesting the amorphous nature of MPC carbon, which agrees with HRTEM in Figure 25b. For MPC-800/Se 50, all the characteristic diffraction peaks related to pure Se disappear. One broad peak is found located at about 25°, implying all Se are buried into the micropores of MPC. Thermogravimetric analysis (TGA) reveals that the Se content in MPC-800/Se 50 is about 48.0 wt% (Figure 27). The above results can be summarized that microporous carbon with high surface area and narrow pore distribution was successfully prepared by direct pyrolysis of PVDF powders without any further activation process. The resulting MPC-800/Se 50 composite shows a uniform distribution of Se in the microporous carbon.



Figure 27. TGA curve of MPC-800/Se 50 performed in an argon environment.

4.2.1 Effect of PVDF carbonization temperature

To obtain the best electrochemical performance for MPC/Se composites, systematic optimization was performed on MPC/Se cathodes in terms of PVDF carbonization temperature, Se loading on the cathode, and Se content MPC/Se. Figure 28 presents the effects of PVDF carbonization temperature and Se loading on MPC/Se cathodes' performance in Li-Se batteries. As seen in BET isotherms (Figure 28a), all MPCs carbonized at 600 °C, 700 °C, and 800 °C exhibits type-I isotherm, which is a typical feature of "microporous solids" [140, 141]. The main difference among these samples is the BET surface area, which is 731.2 m² g⁻¹, 671.3 m² g⁻¹, and 830.0 m² g⁻¹ for MPC-600, MPC-700, and MPC-800, respectively (Table 3). Raman spectra (Figure 28b) of MPC-600, MPC-700, and MPC-800 show two broad distinct peaks at 1345 cm⁻¹ and 1590 cm⁻¹, which are assigned to the D band and G band, respectively [88, 89, 143]. The D band is due to disordered carbon originating from sp³ carbons, whereas the G band is associated with a hexagonal carbon structure. I_D/I_G ratios for all the samples are in a range of 2.4-2.6, suggesting a similar degree of disorder in their carbon structure. Physical characterizations suggest that MPC obtained at different carbonization temperatures have no significant difference in their carbon structure, the type of pore size, and specific surface area.



Figure 28. (a) BET isotherms and (b) Raman spectra of MPC-600, MPC-700, and MPC-800; (c) cycling performance of MPC-600/Se 50, MPC-700/Se 50, and MPC-800/Se 50 with Se loadings of ~ 1.5 mg cm⁻² at 0.1C; (d) 1st cycle charge and discharge curves for MPC-600/Se 50, MPC-700/Se 50, and MPC-800/Se 50; (e) long cycling stability of MPC-800/Se 50 measured at a current density of 0.1C in the first 5 cycles, and 0.5C in the following cycles; and (f) specific and areal capacities of MPC-800/Se 50 electrodes with Se loadings ranging from 1.3 to 2.0 mg cm⁻² (specific and areal capacities are calculated using reversible discharge capacity in the 2nd cycle).

Figure 28c-28f present the electrochemical performance of MPC-600/Se 50, MPC-700/Se 50, and MPC-800/Se 50 cathode in Li-Se batteries based on 1M LiPF₆ in EC: DEC carbonate electrolyte. As seen in Figure 28c, all the cathodes exhibit stable cycle stability over 100 cycles and almost the same reversible capacity of 530 mAh g⁻¹ at 0.1C. Discharge-charge curves of all

the samples in the first cycle are featured with only one plateau at the same potential of 1.7 V – 1.8 V, which suggests a one-step phase change between Se and Li₂Se (Se + $2Li^+ + 2e^- \leftrightarrow Li_2Se$) and agrees well with previous work on Li-Se batteries based on carbonate electrolytes [82, 84-86, 88-90, 134-136]. A one-step phase transition in charge-discharge profiles is one of the main characteristics of Li-Se batteries based on carbonate electrolytes. It suggests that Se is completely buried into the carbon hosts' micropores [17, 95, 118, 137]. This one-step reaction is further confirmed by CV curves (Figure 31), which show one pair of oxidation and reduction peaks located at ~ 1.2 V and 2.2 V, respectively. Coulombic efficiency (CE) in the first cycle is calculated to be 61.3%, 61.0%, and 59.1%, for MPC-600/Se 50, MPC-700/Se 50, and MPC-800/Se 50, respectively. In the following cycles, CE maintains over 99.6 % for all the samples (Figure 29). The results in Figure 28c-28d reveal that although PVDF carbonization temperature affects the specific surface area of MPC to some extent, it has an inappreciable influence on the battery performance of MPC/Se composite cathodes. Since all MPC have mainly micropores in their structure (Figure 28a), it can be concluded that micropores in the carbon play a key role in enabling high specific capacity and excellent cyclic stability for MPC/Se composite cathodes. Long cycling stability of MPC-800/Se 50 is evaluated at 0.1C for 5 cycles and 0.5C for the following cycles and presented in Figure 28e. It can be seen that MPC-800/Se 50 exhibits a reversible capacity of ~ 400 mAh g^{-1} at 0.5C, and ultra-stable cyclic performance for 200 cycles, indicating the superior performance of MPC as a stable Se matrix.

Furthermore, Se loading on the MPC/Se electrode $(1.3-2 \text{ mg cm}^{-2})$ was controlled by adjusting the electrode thickness using a doctor blade, and Se loading on the specific capacity and areal capacity of MPC-800/Se 50 was investigated. As presented in Figure 28f, the specific capacity of MPC-800/Se 50 gradually increases with the Se loading and reaches a maximum of

540 mAh g⁻¹ with a Se loading of 1.6 mg cm⁻². Higher Se loadings decrease the specific capacity, probably due to electrolyte wetting issue in thick electrodes [139, 144]. On the other hand, the specific areal capacity is elevated monotonously with the Se loading and reaches 1.1 mAh cm⁻² with a Se loading of 2.0 mg cm⁻².



Figure 29. Coulombic efficiency (CE) of MPC-600/Se 50, MPC-700/Se 50, and MPC-800/Se 50 measured at 0.1 C.

The above results show that MPC derived from PVDF *via* an activation-free process is an excellent Se host material to enable stable, high capacity, and long-lifetime for Se cathode for Li-Se batteries in carbonate electrolytes. It should be noted that the mechanism of (de)lithiation of Se cathode in carbonate-based electrolytes is quite different from that in ether-based ones [17]. In ether-based electrolytes, Se undergoes multi-step phase transitions during the lithiation and delithiation processes. During the lithiation process, Se will be first reduced to high-order polyselenides Se_n²⁻ (n \geq 4) and then further to Se_n²⁻ (n \geq 4) to Se₂²⁻ and Se²⁻ [17, 60, 95]. The soluble polyselenides in ether-based electrolytes can cause a severe shuttle effect, leading to poor cycling life and low specific capacity of Se cathode [60, 132]. We observed only one plateau in carbonate electrolytes, suggesting only one phase transition during the lithiation and delithiation process for MPC-800/Se 50. The distinguished electrochemical performance in MPC-800/Se 50 could be attributed to the infiltration of Se into interior micropores of MPC, which can 83

effectively confine Se to alleviate the dissolution of polyselenide and reduce the diffusion lengths for Li-ions and electrons [82, 84-86, 89, 90, 134, 135].

4.2.2 Effect of Se content in MPC/Se composites

Se content in MPC/Se composites is a critical factor determining the overall energy density of Li-Se batteries at the system level. Therefore, the effect of Se contents (~ 50 wt%, 60 wt%, and 70 wt%) on the electrochemical performance of MPC/Se cathodes was investigated by using the optimized MPC-800 as a model material.

 N_2 adsorption-desorption isotherms analysis in Figure 30a discloses that the BET surface area of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 significantly decreases to 18.2 m² g⁻¹, 3.0 m² g⁻¹, and 3.5 m² g⁻¹, respectively (Table 3). This result suggests that the micropores in MPC-800 are filled for higher Se contents (MPC-800/Se 60 and MPC-800/Se 70), while a small portion of micropores remain unoccupied for MPC-800/Se 50. Figure 30b reveals that the XRD patterns show that strong and sharp diffraction peaks show up in MPC-800/Se 60 and MPC-800/Se 70 and could be assigned to trigonal Se. This is different from broad peaks for MPC-800/Se 50. The reason could be that for higher Se contents, Se will first fill the micropores of MPC-800, and then the remaining Se stays as "bulk type" on the outer surface of MPC particles. The bulk Se will contribute to the strong XRD diffraction peaks (Figure 30b).



Figure 30. (a) BET and (b) XRD patterns of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70; chargedischarge curves in (c) the 1st cycle and (d) 5th cycle; (e) cycling performance at 0.1C and (f) rate capability of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 measured at different currents (0.1-5C) in a voltage range of 0.5-3V.



Figure 31. CV curves of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 80 measured at a scanning rate of 0.2 $mV s^{-1}$.

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Sample	BET surface area $(m^2 g^{-1})$	Sample	BET surface area $(m^2 g^{-1})$
MPC-600	731.3125	MPC-800/Se 50	18.1728
MPC-700	671.2650	MPC-800/Se 60	2.9451
MPC-800	829.9228	MPC-800/Se 70	3.5337

Table 3. BET surface area of MPC hosts and MPC/Se with different Se contents

Electrochemical properties of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 in Li-Se batteries are compared in Figure 30c-30f. As shown in Figure 30c, the 1st-cycle discharge capacity is 1088.5 mAh g⁻¹, 804.1 mAh g⁻¹, and 635.1 mAh g⁻¹, for MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70, respectively. The higher capacity than the theoretical value of Se (675 mAh g⁻¹) could be attributed to the decomposition of carbonate electrolytes and SEI formation in the 1st cycle [84, 86, 134]. Moreover, the difference between discharge and charge potentials becomes significantly larger with the increased Se content from about ~ 50 wt% to 70 wt% in the MPC/Se composites, as shown in Figure 30c and Figure 30d for the 1st and the 5th cycle. Moreover, the CV analysis (Figure 31) reveals the broadening feature and larger separation between oxidation and reduction peaks with increasing Se contents, suggesting larger polarization and slower kinetics of electrochemical reactions for MPC/Se composites higher Se contents. As a result, the lower cut-off voltage must be extended from 1 V to 0.5 V for electrochemical testing of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 complete the full lithiation reaction from Se to Li₂Se. As shown in Figure 33, MPC-800/Se 60 and MPC-800/Se 70 only deliver specific discharge capacities of 500 mAh g⁻¹ and 350 mAh g⁻¹, respectively, in the 1^{st} cycle voltage range of 1V - 3V. This result shows that larger overpotential is required to initiate and complete the lithiation reaction for MPC/Se cathodes with higher Se contents. It is worth noting that a small plateau between 2 V and 1.5 V is observed in the 1st-cycle discharge curve of MPC-800/Se 60 and MPC-800/Se 70 (Figure 33) and is assigned 86

to the dissolution of bulk Se into carbonate electrolytes in previous studies [82, 84, 85]. However, we did not observe the same phenomena in MPC-800/Se 50 (Figure 30c). The cycling stability and rate capability of MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 are shown in Figures 30e and 30f, respectively. MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 maintain reversible capacities of 583.4 mAh g⁻¹, 442.3 mAh g⁻¹, and 292.9 mAh g⁻¹ over 100 cycles, with average CE over 99.5% from the 2^{nd} to the 100^{th} cycle (Figure 30). The rate capability measured at 0.1C -5C decreases in the order of MPC-800/Se 50 > MPC-800/Se 60 > MPC-800/Se 70 (Figure 30f). For example, MPC-800/Se 50 could deliver a specific capacity of 350.3 mAh g⁻¹ at 2C, while the reversible capacity is only 245.1 mAh g⁻¹ and 150.1 mAh g⁻¹ for MPC-800/Se 60 and MPC-800/Se 70, respectively. The charge-discharge profiles and XRD analysis (Figure 30b, Figure 30c, and Figure 30) strongly indicate that bulk Se exists in MPC-800/Se 60 and MPC-800/Se 70, but MPC-800/Se 50, and that the increasing Se content and unconfined Se (or bulk Se) result in the capacity loss for MPC-800/Se 60 and MPC-800/Se 70.



Figure 32. CV curves of (a) MPC-800/Se 50 and (b) MPC-800/Se 70 measured at 0.1. 0.2. 0.3. 0.5 and 0.6 mV s-1 between 0.5 V and 3.0 V; (c) linear fit of peak currents as a function of square root of scan rates obtained in (a) and (b).

To develop a better understanding of the Se content effect on the electrochemical properties of MPC/Se composites, the CV curves for MPC-800/Se 50 and MPC-800/Se 70 are measured at various scan rates from 0.1 mV s^{-1} to 0.6 mV s^{-1} and showed in Figure 32a and 32b.

It can be found that the peak current is proportional to the square root of scan rates (Figure 32c), indicating that the electrochemical reaction (Se + Li⁺ + e⁻ \leftrightarrow Li₂Se) is diffusion-controlled. The Li-ion diffusion coefficients (D_{Li}⁺) are determined according to the Randles-Sevcik equation [145, 146]:

$$I_p = 2.69 \times 10^5 n^{3/2} AD^{1/2} v^{1/2} C = B \times v^{1/2}$$
 (Equation 1)

Where I_p is the peak current, n is the number of electrons involved in the reaction, A is the electrode area, C is the concentration of Li ions in the electrolyte, and B is the slope of the best-fit-curve in Figure 32c. D_{Li}^+ is calculated to be 5.97×10^{-11} cm² s⁻¹ (cathodic) and 5.84×10^{-11} cm² s⁻¹ (anodic) for MPC-800/Se 50, and 5.29×10^{-12} cm² s⁻¹ (cathodic) and 5.86×10^{-12} cm² s⁻¹ (anodic) for MPC-800/Se 70. This result suggests that D_{Li}^+ in MPC/Se composite cathode is associated with the Se content, and higher Se content in MPC/Se composites leads to a decrease in Li-ion diffusion rate. This explains the electrochemical performance difference among MPC-800/Se 50, MPC-800/Se 60, and MPC-800/Se 70 (Figure 30). The reduced Li-ion diffusion rate in MPC-800/Se 70 might result from the accumulation of bulk Se on MPC particles' outer surface. The bulk Se could block the access of Li ions from electrolytes to Se in the micropores of MPC, therefore slowing down the electrochemical reaction in MPC/Se composites.



Figure 33. Charge-discharge profile for higher loadings of selenium in a voltage range of 1-3 V.

The above systematic study shows that micropores and micropore volume are the key merits for porous carbon as Se host for Li-Se batteries based on carbonate electrolytes. Microporous carbon can effectively constrain Se in the space and prevent its dissolution into carbonate electrolytes during 1st discharge process, leading to highly reversible capacity and good cycling stability in Se cathodes [82, 84-86, 89, 90, 134, 135]. In contrast, Se hosted in mesopores and macropores of the carbon is generally irreversible, as evidenced by irreversible and higher discharge plateau in the 1st cycle in our work (Figure 33) and others' results [82, 84, 85]. Therefore, it is critical to developing a porous carbon matrix with dominant microporous and high micropore volumes to maximize Se content in the Se composite cathodes. To reach 80wt% of Se content in the Se composite, the carbon matrix's micropore volume needs to get ~ 0.9 cm³ g⁻¹ (Figure 34), which is still quite challenging and requires a different process and material developments.



Figure 34. Theoretical calculation of Se content in Se composites as a function of micropore volume in the carbon matrix.

A detailed comparison between this work and previous studies on Se cathode based in carbonate electrolyte is made, in terms of the synthesis process, micropore volume, Se loading, Se content, and electrochemical performance (Table 4). As a Se host material, MPC synthesized by one-step pyrolysis of commercial PVDF shows comparable electrochemical performance as nanostructured carbon fabricated *via* sophisticated and multi-step processes, such as ZIF-8 and MOF derived microporous carbon and CMK-3, *etc*. The simplicity of the MPC synthesis process is an advantage for scaling up towards practical applications.

In summary, microporous carbon (MPC) with the high surface area was successfully prepared by direct pyrolysis of PVDF in one step and used as a host material for Se cathode in Li-Se batteries. The results suggested that micropores in MPC were the determinant factor for affecting MPC/Se composites' performance. Carbonization temperatures for PVDF had a negligible influence on the micropores and electrochemical performance of MPC/Se cathodes. Se contents in MPC/Se composites significantly affected the specific capacity and rate capability of MPC/Se cathodes. Increasing Se content from ~ 50 wt% to 70 wt% led to reduced reversible capacity from 583.4 mAh g⁻¹ to 292.9 mAh g⁻¹ for MPC/Se cathode. The reason was attributed to bulk Se sitting outside of micropores, which reduced the Li-ion diffusion coefficient in MPC/Se. The optimal MPC/Se cathode delivered a reversible capacity of 530 mAh g⁻¹ at a current density of 0.1 C. It exhibited an areal capacity up to 1.1 mAh cm⁻² with a Se loading of 2 mg cm⁻². The exceptional cyclability of MPC/Se cathodes was mainly due to the uniform distribution of Se in micropores, which could alleviate side reactions with electrolytes and prevent the dissolution of polyselenides in carbonate electrolytes.

Table 4. Comparison of Se cathode in Li-Se batteries based on carbonate electrolytes.

Cathode	Synthesis method for porous carbon	Se content (wt%)	Microporous volume (cm ³ g ⁻¹)	Electrolyte	Se loading (mg cm ⁻²)	Performance	Ref.
3D interconnected mesoporous carbon nanofibers-Se	Electrospinning of PAN, carbonization, KOH activation	52.3%	N/A	1M LiPF ₆ , EC:DEC	0.8	$\begin{array}{c} 643 \text{ mAh } \text{g}^{-1} (100^{\text{th}} \\ \text{cycle}), \text{ at } 50 \text{ mA } \text{g}^{-1} \\ (0.07\text{C}) \end{array}$	[82]
ZIF-8 derived microporous carbon/Se	Synthesis of ZIF-8, carbonization of ZIF- 8 followed by HCl washing	51.4%	0.76	1M LiPF ₆ , EC:DMC	N/A	485 mAh g^{-1} (100 th cycle), at 1C	[134]
ZIF-8 derived microporous carbon/Se	Synthesis of ZIF-8, carbonization of ZIF- 8 followed by HCl washing	51%	0.474	1M LiPF ₆ , EC:DEC	N/A	500 mAh g^{-1} (2 nd cycle), at 0.1C	[86]
MOF-derived porous carbon/Se	Carbonization of Al-MOF, HF washing to remove Al	50% 60%	0.358	1M LiPF ₆ , EC:DEC	N/A	605 mAh g^{-1} (10 cycle), at 0.1C 500 mAh g^{-1} (10 cycle), at 0.1C	[84]
N-doped microporous carbon/Se	Carbonization of polypyrrole spheres, KOH activation	50%	0.54	1M LiPF ₆ , EC:DEC:DMC	2	570 mAh g ⁻¹ (350 cycle), at 0.5C	[85]
Doube-shell N-doped carbon nanobelts	Hydrothermal synthesis of ZnSe (DETA) _{0.5} , carbonization of ZnSe(DETA) _{0.5} followed by washing with FeCl ₂ aqueous solution	62.5%	N/A	1M LiPF ₆ , EC:DEC	3	597.4 mAh g ⁻¹ , at 0.12C	[135]
Se/mesoporous carbon	Solution-method synthesis of spherical precursors followed by carbonization	30%	0.2	1M LiPF ₆ , EC:DEC	N/A	480 mAh g ⁻¹ (1000 cycle), at 0.25C	[90]
CMK-3/Se	Synthesis of SBA-15 template, synthesis of CMK-3 followed by carbonization and HF washing to remove SBA-15 template	49%	0.131	1M LiPF ₆ , EC:DMC	N/A	600 mAh g ⁻¹ (50 th cycle), at 0.1C	[89]
Porous carbon nanospheres	Hydrothermal synthesis of spherical precursors, followed by carbonization	70.5%	N/A	1M LiPF ₆ , EC:DMC	2	605 mAh g ⁻¹ , at 0.2C	[88]
Carbonized polyacrylonitrile–Se (PAN-Se)		36%	N/A	1M LiPF ₆ , EC:DEC	N/A	600 mAh g ⁻¹ , at 0.3C	[136]
MPC/Se		50% 60% 70%	0.35	1M LiPF ₆ , EC:DEC	1.2-2	600 mAh g ⁻¹ , at 0.1C 500 mAh g ⁻¹ , at 0.1C 300 mAh g ⁻¹ , at 0.1C	This work

Chapter 5: High-Performance Sodium-Selenium Batteries Enabled by Microporous Carbon/Selenium Cathode and Fluoroethylene Carbonate Electrolyte Additive[‡]

This chapter is the following work done after optimization of microporous carbon, which has been done in chapter 4. In the previous chapter, the microporous carbon was elaborated in regards to the carbonization temperature, and the MPC/Se composite was then improved in terms of selenium content and loading. The MPC-800/Se 50 showed the best electrochemical performance in Li-Se batteries, and it was a time to elevate the work to a different level and investigate the optimized composite in Na-Se batteries. Sodium-selenium (Na-Se) batteries are promising energy storage systems due to their relatively low cost and high volumetric energy density of Se cathode. However, the practical application of Na-Se batteries has been hindered by the polyselenides dissolution (or shuttle effect phenomena), which could cause low Coulombic efficiency and poor cycling lifetime. Therefore, this work was limited to the analysis of the capacity performance of the same composite structure in Na-Se batteries and the effect of electrolyte composition was investigated on the capacity retention and cycle ability of the composite enhanced in the former sub-project. Herein, we addressed the polyselenides dissolution by using microporous carbon (MPC) derived from poly (vinylidene fluoride) as the Se host and fluoroethylene carbonate (FEC) as the additive in the electrolyte. The MPC/Se cathode with 3% FEC additive maintained a specific capacity of 382 and 350 mAh g⁻¹ in the 100th and 200th cycle, respectively.

In contrast, the MPC/Se cathode without FEC could only deliver 317 and 245 mAh g⁻¹

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CRediT authorship contribution statement

Mohammad Hossein Aboonasr Shiraz: Conceptualization, Investigation, Writing - original draft. Peter Zhao: Visualization, Validation. Jian Liu: Supervision

after 100 and 200 cycles, respectively. Another important finding was that the use of FEC additive could prevent the corrosion of Na metal anode from soluble polyselenides and preserve Na's structural integrity, contributing to the enhanced cycling stability and specific capacity of Na-Se batteries. It is expected that this work could draw researchers' attention to the importance of reporting and studying Na metal anode while optimizing Se cathode for Na-Se batteries.

Rechargeable lithium-ion batteries (LIBs) play a critical role in portable devices, electric vehicles, and large-scale stationary energy storage due to their relatively high energy density and low cost among available technologies [96]. However, current LIBs are gradually approaching their theoretical limit due to the intercalation battery chemistry and active materials employed [7, 147]. Moreover, it has been widely recognized that the limited Li reserve might pose challenges for the rapidly growing market for LIBs. Recently, sodium-based batteries have attracted increasing research attention as promising alternatives to LIBs, owing to the wide availability and low cost of sodium precursors [148-151].

Sodium-Sulfur (Na-S) batteries have attracted increasing research attention due to the high specific capacity of sulphur (1672 mAh g⁻¹), and large abundance, and low cost of sulphur [152]. High-temperature Na-S batteries have been developed in 1967 by Ford Motor Company and are commercially available today. High-temperature Na-S batteries operate over 300°C to keep sodium anode and sulphur cathode in the liquid state and employ β -alumina solid electrolyte to ensure high ionic conductivity [153]. However, molten Na-S cells' operation causes multiple technological challenges, such as safety, lack of specialized sealing for high-temperature operation, system maintenance, and reliability. In response to these challenges, research on room-temperature Na-S batteries had been stimulated since 2006. There has been significant progress made so far on room-temperature Na-S batteries thanks to the knowledge and concepts

developed in Li-S batteries [154-156]. Nevertheless, room-temperature Na-S batteries still face significant technical problems, such as low conductivity, low utilization, and considerable volume change of active sulphur material, severe shuttle effect, mainly due to the intrinsic nature of insulting sulphur [157].

Recently, elemental selenium (Se), a chemical analog of sulphur (S), has been considered as a promising cathode material for rechargeable sodium-based batteries due to its high electronic conductivity of 1 ×10 $^{-3}$ S m⁻¹ (vs. 5 ×10 $^{-28}$ S m⁻¹ for S) and high volumetric capacity of 3254 mAh cm⁻³ (vs. 3467 mAh cm⁻³ for S) [30, 158, 159]. However, bulk Se still has a relatively large bandgap (1.46 eV) and shows sluggish reaction kinetics, large polarization, and low electrochemical utilization in batteries [160]. To over these problems, confinement of Se into porous carbon has been the predominant and practical approach to improve the electronic and ionic conductivities, cycling performance, and Coulombic efficiency of Se cathode [118, 137, 161]. For example, an early work by Wang et al. [90] prepared Se/mesoporous carbon at a temperature of 600 °C under vacuum. The Se/mesoporous carbon cathode delivered an initial capacity of 485 mAh g⁻¹. They retained 340 mAh g⁻¹ after 380 cycles in Na-Se batteries. Yu et al. [82] developed a free-standing porous carbon nanofibers/Se composite electrode (Se@PCNFs). When used in Na-Se batteries, the composite electrode exhibited a reversible capacity of 520 mAh g⁻¹ after 80 cycles at 0.05A g⁻¹ and a rate capability of 230 mAh g⁻¹ at 1 A g⁻¹. Recently, various metal-organic frameworks (MOF), such as zinc-glutamate MOF [126], ZIF-67 [127, 128], have been used as precursors to synthesize porous carbon as host materials for Se cathodes in Na-Se batteries. The MOF-derived porous carbon possessed narrow pore distribution and high pore volume, which are desirable characteristics of carbon hosts for Se cathodes [162]. Moreover, several studies have used the KOH chemical activation approach to create micropores in cellulose-derived carbon nanosheets [96], self-interwoven carbon nanofiber [70], poly dopamine [163], and then applied the microporous carbon to enable stable and highperformance Se cathodes in Na-Se batteries in carbonate-based electrolytes. Nevertheless, the synthesis for porous carbon in the previous works involved expensive precursors and complex processes, making them difficult for large-scale applications. It is worth noting that, although the performance of Se cathode has been significantly improved by using the Se confinement strategy, the polyselenide shuttle effect still occurs in the Se cathodes even in carbonate-based electrolytes [104, 125, 163]. During cycling, Se might dissolve in the carbonate-based electrolytes, producing high-order polyselenides. The high-order polyselenides can diffuse to the Na anode and deposit on the Na metal as insoluble Na₂Se and Na₂Se₂, or form low-order polyselenides that will move back to the cathode [73]. Recently, electrochemistry and theoretical calculation by Goodenough et al. [29] found that during the first discharge process, Se in microporous carbon underwent a step-wise reduction to Na₂Se, with the formation of intermediate Na₂Se_x in Na-Se batteries. In contrast, the same Se cathode in Li-Se batteries, experienced a single-step electrochemical conversion from Se to Li₂Se. The different reaction mechanisms might be caused by the larger ionic radius of Na⁺ (102 pm) than Li⁺ (74 pm). Therefore, it might require multiple strategies to obtain stable and high-capacity Se cathodes for Na-Se batteries.

Despite many works done on Se cathode, few studies have paid attention to the Na anode in Na-Se batteries. In sodium-ion batteries, it has been well recognized that Na metal faces several challenges, including the formation of Na dendrites, low Coulombic efficiency, and poor cycling performance [164-166]. It remains an open question about the influence of Na metal on the electrochemical performance of Na-Se batteries. It is speculated that the polyselenide shuttle effect and highly reactive Na metal might complicate Na-Se batteries' situation.

Herein, we prepared microporous carbon (MPC) by direct pyrolysis of polyvinylidene fluoride (PVDF) at 800 °C and applied the MPC as a Se host to produce MPC/Se cathode for Na-Se batteries in a carbonate-based electrolyte (1M NaClO₄, EC: DEC). It was found that, by adding FEC additives (3-10%) in the electrolyte, the MPC/Se cathode exhibited greatly improved cycling performance, Coulombic efficiency, and lifetime, in comparison to that without FEC. Mechanistic studies revealed that the FEC additive created stable solid electrolyte interphase (SEI) on the cathode surface to suppress polyselenides dissolution and shuttle effect and resulted in the formation of smooth and dense Na metal anode. In contrast, without FEC additives, the dissolved polyselenides led to the loss of Se active material and resulted in an uneven and porous Na metal anode. Surprisingly, it was also found that the porous Na metal anode became the limiting factor for the performance of Na-Se batteries. Therefore, the outstanding electrochemical performance of Na-Se batteries is reached by using both Se confinement and FEC additive strategies. This work suggests that future work should also report details on the Na metal anode to understand better the interaction between Se cathode and Na metal anode and comprehensively evaluate the actual merits of Na-Se batteries.

5.1.1 Preparation of MPC and MPC/Se composites

Direct carbonization of poly (vinylidene fluoride) (PVDF, (-CH₂CF₂-)_n, MW: 64.035 g mol⁻¹, Alfa Aesar) was conducted in a tube furnace (Lindberg/Blue M Mini-MiteTM) with a heating rate of 10 °C min⁻¹ to reach the desired temperature of 800 °C and then kept for 1h under the inert nitrogen gas environment (99.999%). The pyrolysis temperature (800 °C) of PVDF was optimized previously to yield MPC with the highest specific surface area and micropore volume. By decomposing PVDF, toxic HF gas will be released, making a porous black carbon product

named microporous carbon and no additional activation treatment was done for this carbon host. In the carbonization process, the stainless steel boat was used for holding PVDF, along with the addition of calcium carbonate solution in the outlet to neutralize the released HF gas. After the MPC preparation, the composite of MPC/Se composite has been prepared by a facile melting diffusion method. Se (-100 mesh, 99.5%, Sigma Aldrich) and MPC with a weight ratio of 50:50 were mixed in a planetary ball mill for 1h and then transferred to a sealed stainless steel autoclave under the protection of argon gas (99.999%), followed by heating up to 260 °C for 12 h, making the selenium diffuse into carbon micropores to obtain MPC/Se.

5.1.2 Electrochemical measurements of MPC/Se cathode

Electrochemical measurements were conducted in CR 2032 coin cells using MPC/Se as the cathode and Na metal as the counter electrode. The MPC/Se electrode slurry was prepared with a combination of 80 wt% of MPC/Se composite, 10 wt% of carbon black, and 10 wt% of sodium alginate (in 0.5 wt% aqueous solutions) followed by casting on an aluminum foil using a doctor blade. The MPC/Se electrode was put in a vacuum oven and dried at 50 °C overnight. After that, the electrode was cut into round disks with diameters of 0.5 inch, and with Se loading in a range of 1.0 - 2.2 mg cm⁻². Coin cells were assembled in an argon (99.999%) filled glovebox workstation with H₂O and O₂ levels below 0.1 ppm. Each coin cell consists of one MPC/Se cathode, one Na metal anode, and a glass fibre separator. The thickness of Na metal was ~ 284 μ m. The electrolytes used were 1M NaClO₄ in ethylene carbonate:diethyl carbonate (EC:DEC, 1:1, v/v), with the addition of FEC additives (0, 3, 5, 10, and 15 vol.%). The cycling performance of the coin cells was tested in the voltage window of 0.5 to 3 V on a Neware BTS 4000 battery testing system. Cyclic voltammetry (CV) testing was performed on a Biologic VSP Potentiostat/

5.2 **Results and Discussion**

Figure 35 presents the physical properties of MPC and the MPC/Se composite prepared by the melting diffusion method. The as-prepared MPC has irregular shapes and sizes ranging from 30 µm to 150 µm (Figure 35a). HRTEM characterization discloses the highly disordered structure of MPC (Figure 36). After Se impregnation, the MPC/Se composite maintains the morphology of MPC (Figure 35b). EDS mapping of Se and C elements confirms the uniform distribution of Se in the MPC host, as shown in Figure 35b. Brunauer-Emmett-Teller (BET) analysis indicates that the MPC possesses a specific surface area of 830.0 m² g⁻¹ and a pore volume of 0.39 cm³ g⁻¹. The adsorption-desorption curve of MPC (Figure 35c) exhibits type-I isotherm with microporous solids' characteristics [96], suggesting the dominance of micropores in MPC. In comparison, the MPC/Se composite has a specific surface area of only 18.2 m² g⁻¹ and no detectable pore volume, implying that the micropores in MPC are entirely occupied with Se. XRD patterns in Figure 35d disclose that the MPC/Se composite exhibits a broad diffraction peak at ~ 25 °C, confirming Se in the MPC's micropores. Also, a small peak is observed at 29.6° in the XRD pattern of MPC/Se composite, and is assigned to the (101) plane of trigonal Se (JCPDS No. 06-0362). This might be due to the trace amount of bulk Se residing in the mesopores and MPC/Se composite surface.



Figure 35. (a) SEM image of microporous carbon; (b) SEM image and EDS elemental mapping of the MPC/Se composite; (c) BET results and (d) XRD patterns of MPC and the MPC/Se composite.

Se content in the MPC/Se composite is determined to be 48 wt% by TGA (Figure 37). The TGA was conducted to investigate the Se content. The result showed the Se content of about 48 wt% in the MPC/Se composite. The two stages of weight losses in the TGA curve, i.e., 350–600 °C and 600–900 °C, could be due to the evaporation of Se in mesopores and micropores, respectively, because of the different binding energy between Se and C.



100 MPC/Se 50 48% 60 20 0 0 100 200 300 400 500 600 700 800 900 Temperature (°C)

Figure 36. HRTEM image of microporous carbon (MPC).

Figure 37. TGA curve of the MPC/Se composite.



Figure 38. (a) Cycling performance, (b) rate capability, (c, d) CV curves (Se loading: 1.2 mg cm⁻²) in 1M NaClO₄, EC:DEC electrolytes with and without 3% FEC additive.

Figure 38a presents the MPC/Se cathode's cycling stability in Na-Se batteries using 1M NaClO₄, EC: DEC electrolyte with and without 3% FEC at 0.1C (1C = 678 mA g⁻¹). Without FEC additive, the MPC/Se cathode delivers a specific discharge capacity of 853 mAh g⁻¹ in the first cycle. The higher capacity than the theoretical value of Se (678 mAh g⁻¹) might be due to the decomposition of electrolytes and the formation of solid electrolyte interphase (SEI) [134]. During the subsequent cycles, MPC/Se cathode's specific capacity gradually decays and reaches 317 and 245 mAh g⁻¹ after 100 and 200 cycles, respectively. In comparison, MPC/Se cathode exhibits enhanced cycling stability with a 3% FEC additive. For example, it can maintain a specific capacity of 382 and 350 mAh g⁻¹ in the 100th and 200th cycle, respectively, in the 3% FEC-containing electrolyte. Moreover, the addition of an FEC additive in the electrolyte

enhances the MPC/Se cathode's rate capability. As shown in Figure 38b, the MPC/Se cathode displays a reversible capacity of 519 mAh g⁻¹, 448 mAh g⁻¹, 389 mAh g⁻¹, 330 mAh g⁻¹, and 245 mAh g⁻¹ in the EC:DEC electrolyte, and 544 mAh g⁻¹, 479 mAh g⁻¹, 419 mAh g⁻¹, 368 mAh g⁻¹, and 309 mAh g⁻¹ in 3% FEC, EC:DEC electrolyte, at a current density of 0.1C, 0.2C, 0.5C, 1C, and 2C, respectively. It is evident that the FEC additive in the EC: DEC electrolyte improves the cycling stability, specific capacity, and rate capability of MPC/Se cathode in Na-Se batteries. Furthermore, FEC contents (0-15%) on the electrochemical performance of MPC/Se cathode are also studied in detail. Overall, 3-10% FEC shows similar improvement in the cycling stability and rate capability of the MPC/Se cathode in Na-Se batteries (Figure 38). Higher FEC content (15%) still enhances the cycling stability but has a negligible effect on the MPC/Se cathode's rate capability. It was observed that 15% FEC-containing electrolyte had poor wettability on the glass fibre separator and the MPC/Se cathode, which might affect the performance at high rates. Thus, it can be concluded that the FEC content in EC: DEC electrolyte is 3-10% (volume ratio) to obtain the optimal specific capacity, cycling stability, and rate capability of the MPC/Se cathode for Na-Se batteries.

Electrochemical properties of the MPC/Se composites with higher Se content (MPC/Se 60, MPC/Se 70) in Na-Se batteries are compared in Figure 44a-d. For both MPC/Se 60 and MPC/Se 70, the discharge capacity is higher in the cell with FEC electrolyte additive, implying FEC's effect in improving the electrochemical performance. Also, FEC's impact on the cycling performance stability of the cell is much more evident for the MPC/Se 70 cathode. As shown in Figure 44b, the MPC/Se 70 electrode's capacity starts to fade from the second cycle with the electrolyte of 1M NaClO₄ EC-DEC; however, for the cell with 3% FEC, relatively stable and reversible capacity could be observed. The results concluded that among different Se content in

MPC/Se composite, MPC/Se 50 is the optimum one, which further electrochemical investigation should be focused on.

To find out the reasons for the improved performance by FEC additive, CV analysis was performed on the MPC/Se cathode at a scan rate of 0.2 mV s⁻¹, and the results in the first five cycles are shown in Figure 38c-38d. In the EC: DEC electrolyte, MPC/Se cathode exhibits a broad reduction peak at about 0.5V and one oxidation peak at ~ 1.5V in the first cycle. Notably, the MPC/Se cathode shows two reduction peaks located at 1.0V and 0.8V in the second cycle and 0.9V and 0.5V in the third cycle, indicating two-step phase change reactions between Se and Na during the sodiation process [167]. During the sodiation process, Se turns into intermediate phase Na₂Se_n ($n \ge 4$) in the first step, and then Na₂Se_n ($n \ge 4$) converts to the final Na₂Se phase in the second step [30]. From the fourth cycle forward, there is one strong reduction peak appearing at about 0.9V for the MPC/Se cathode. Besides, one small shoulder reduction peak starts to evolve at 1.35V after the 2nd cycle and can be attributed to the formation of soluble intermediate phase Na₂Se_n ($n \ge 4$). Nevertheless, the oxidation process shows only one peak at ~ 1.7V all the time, suggesting direct phase transformation from Na₂Se to Se during the disodiation processes [73, 168]. In comparison, in 3% FEC-containing electrolyte, MPC/Se cathode displays two reduction peaks and one oxidation peak during the first four cycles (Figure 38d), similar to those observed in the EC: DEC electrolyte albeit difference in the peak potentials. It is noted that, in the 5th cycle, the MPC/Se cathode exhibits only one reduction peak at 1.1V, and no other peak is detected in the CV curve (Figure 38d). Additionally, the separation between oxidation and reduction peaks of MPC/Se cathode is reduced from 0.8V to 0.6V in the 5th cycle with FEC additive, indicating better kinetics in MPC/Se cathode in the FEC-containing electrolyte. The comparison between Figures 38c and 38d suggests that the FEC additive effectively suppresses

the dissolution of polyselenides from MPC/Se cathode into the carbonate electrolyte, probably due to the formation of stable SEI on the MPC/Se cathode via the decomposition of FEC [169]. In sodium-ion batteries, FEC additive has been reported to induce the formation of a thin and stable protective layer on the electrode, leading to a significant improvement in the cyclability [166]. In particular, the FEC additive in the electrolytes was crucial for alloying- and conversion-type electrodes, which accompanied dramatic volume changes upon the sodiation-desodiation process.



Figure 39. The effect of FEC contents (0, 3, 5, 10, and 15 vol.%) on the (a, c) cycling stability and (b, d) rate capability of the MPC/Se cathode in Na-Se batteries using 1M NaClO₄, EC: DEC electrolyte.

The charge/discharge curves of MPC/Se composite with and without FEC at different cycles (1st, 2nd, 3rd, 5th, 10th, 0.1 C) and different rates (0.1, 0.2, 0.5, 1, 2 C) were depicted in

Figure 40. In charge-discharge profiles at different cycles (Figure 40a and 40b), from the second cycle, the charge and discharge profiles in both cells contain EC-DEC and EC-DEC, 3% FEC in the electrolyte showed a good overlapping, indicating the reversibility of the sodiation/desodiation phenomenon. This overlapping becomes much more evident for the FEC electrolyte additive cell, indicating FEC's effect on the performance of the cell. Moreover, from the charge/discharge profiles at different rates (Figure 40c and 40d), it was concluded that the polarization of the MPC/Se was decreased in the cell contains FEC electrolyte additive. The improved capacity and kinetics in EC-DEC, 3% FEC electrolyte could result from the protective effect of SEI layer derived from FEC, which alleviates polyselenide dissolution and reduces the deposition of solid polyselenides.



Figure 40. (a, b) The charge/discharge curves of MPC/Se composite with and without FEC at different cycles (1st, 2nd, 3rd, 5th, 10th, 0.1 C) and (c, d) different rates (0.1, 0.2, 0.5, 1, 2 C).



Figure 41. CV curves of MPC/Se cathode in Li-Se batteries using 1M LiPF₆ EC: DEC (1:1 volume ratio) electrolyte.

An interesting comparison was made for the MPC/Se cathodes in Na-Se batteries (1M NaClO₄, EC: DEC) and Li-Se batteries (1M LiPF₆ EC: DEC). In Li-Se batteries, MPC/Se cathode exhibits only one reduction peak and one oxidation peak in the first 5 cycles (Figure 41), indicating a one-step electrochemical reaction between Li and Se ($2Li^+ + Se + 2e^- \leftrightarrow Li_2Se$) [162]. Moreover, both reduction peaks and oxidation peaks after the 1st cycle have good overlaps in peak potential and current, suggesting the excellent reversibility of MPC/Se cathode In Li-Se batteries. In contrast, MPC/Se cathode shows a step-wise reduction process with the formation of soluble intermediate polyselenides in 1M NaClO₄, EC: DEC electrolyte (Figure 40c). The difference between MPC/Se cathode behaviours in Li-Se and Na-Se batteries might be due to the larger ionic radius of Na⁺ (102 pm) slows down the sodiation process. Initially, sodiated Se might block the transport of Na⁺ in the microporous carbon [29].



Figure 42. Nyquist plots of the MPC/Se cathode after 200 cycles in EC: DEC electrolytes with and without 3% FEC additive (insert shows the equivalent circuit model used for fitting the experimental impedance).

Electrochemical impedance spectroscopy (EIS) was used to evaluate MPC/Se cathode resistance after 200 cycles in EC: DEC electrolytes with and without 3% FEC additive, and the results are plotted in Figure 42. The resistance parameters were obtained by fitting the EIS results using the equivalent circuit model (Insert in Figure 42). R_{el} represents electrode and

electrolyte impedances, while R_{ct} stands for charge transfer resistance at the cathode-electrolyte interface. MPC/Se cathode shows a R_{el} of 5.5 Ω and a R_{ct} of 272.2 Ω without FEC, and a R_{el} of 5.4 Ω and a R_{ct} of 190.5 Ω with 3% FEC additive. The much smaller R_{ct} in the latter indicates that MPC/Se cathode is much more stable in FEC-containing electrolyte than in FEC-free ones over long-term cycling, probably due to the thin and tough SEI induced by FEC decomposition [70].



Figure 43. (a,b) top-view and (c,d) cross-sectional view SEM images of sodium metals recycled after 200 cycles from the Na-Se cells with and without FEC additive. The scale bar is 100 μm.



Figure 44. Cycling performance and Coulombic efficiency of (a, c) MPC/Se 60 and (b, d) MPC/Se 70 at 0.1 C in 1M NaClO₄, EC: DEC electrolytes with and without 3% FEC additive.

To further examine the electrodes after cycling, the morphologies of glass fibres and Na metals after 200 cycles were observed by SEM. The typical images are presented in Figure 43 and Figure 46. Figure 43 reveals a pronounced difference of sodium morphologies between FEC-containing and FEC-free electrolytes after battery cycling. In the FEC-free electrolyte, the sodium metal is rough and spongy (Figure 43a and 43c) and turns into a reddish colour (insert Figure 43a). This observation suggests severe parasitic reactions between soluble polyselenides and metallic sodium anode during the charge/discharge processes, causing the deposition of solid Na₂Se₂ and Na₂Se [104].

In contrast, In the FEC-containing electrolyte, the sodium metal becomes smooth and compact with a grey colour (Figure 43b and 43d), indicating the less deposition of solid polyselenides on the sodium metal. Moreover, the glass fibre separator recycled from the Na-Se cell with FEC-free electrolyte is yellowish, in contrast to the white colour of glass fibre 108
recovered from FEC-containing electrolyte (Figure 46). The colour change in the separator in the FEC-free electrolyte is mainly due to the polyselenide diffusion from MPC/Se cathode to the sodium metal anode over the repeated cycling. The results in Figure 43 and Figure 46 reveal that the FEC additive effectively suppresses the polyselenide dissolution from the MPC/Se cathode. It reduces the loss of active Se material and preserves the structural integrity of sodium metal anode by reducing solid polyselenide deposition and avoiding the formation of spongy Na metal. In Na-ion batteries, FEC additive was found to help form NaF-rich SEI on the sodium metal and limit sodium metal's reactivity with carbonate electrolytes, suppressing the Na dendrite growth and improving its Coulombic efficiency and lifespan [165, 170].



Figure 45. Cycling performance of (a) MPC/Se cathodes with different Se loadings (1.2, 1.8, and 2.2 mg cm⁻²) at 0.1C in the EC:DEC electrolyte, and (b) the MPC/Se cathode with 2.2 mg cm⁻² Se loading in 3% FEC, EC:DEC electrolyte.

Se loading (mg cm⁻²) is a critical factor for Na-Se batteries because it determines the areal capacity (mAh cm⁻²) of the Se cathode and the overall energy density of Na-Se batteries. The effect of Se loading on the cycling performance of MPC/Se cathode was initially investigated in the FEC-free electrolyte at 0.1C. As shown in Figure 40a, the increase of Se loading from 1.2 to 1.8 and 2.2 mg cm⁻² leads to increased areal capacity from ~ 0.7 to 1.1 and 1.2 mAh cm⁻², respectively, in the second cycle. All the MPC/Se cathodes exhibit gradual capacity degradation over long-term cycling due to the polyselenide dissolution and Na corrosion, as observed in

Figures 37c and 43a, 43c. Surprisingly, the MPC/Se cathode with Se loadings of 1.8 and 2.2 mg cm⁻² show a sudden capacity drop in the 180th cycle and 55th cycle, while the one with the lowest loading of 1.2 mg cm⁻² lasts for 300 cycles with an areal capacity of ~ 0.3 mAh cm⁻². There is a clear dependence on the lifespan of the MPC/Se cathode on Se loading. When all the MPC/Se cathodes are cycled at 0.1C, the current density per area is calculated to be 0.08, 0.12, and 0.15 mA cm⁻² for Se loadings of 1.2 to 1.8 and 2.2 mg cm⁻², respectively. To find out the cause for sudden cell failure, MPC/Se cathode with Se loading of 2.2 mg cm⁻² was recycled from the Na-Se cell after 100 cycles and re-assembled with a fresh Na metal during the testing. As shown in Figure 45a, the re-assembled Na-Se cell could recover an areal capacity of ~ 0.7 mAh cm⁻² and continue the trend of MPC/Se cathode. This experiment indicates that the sudden capacity drop in Na-Se cells with higher Se loadings was mainly due to the Na metal anode's failure rather than the MPC/Se cathode. As shown in Figures 43a and 43c, without FEC additive, the Na metal anode was eroded owing to its high reactivity with carbonate electrolyte and polyselenides. With higher Se loading, the increased areal current density is likely to cause more severe Na dendrite growth [165], which accelerates the erosion of Na metal in Na-Se batteries. It would explain the shortened lifespan of Na-Se cells with higher Se loadings (1.8 and 2.2 mg cm⁻²). Figure 45b presents the MPC/Se cathodes' cycling performance with the highest Se loading (2.2 mg cm⁻²) in the FEC-free and FEC-containing electrolytes. It can be seen that the MPC/Se cathode exhibits a stable reversible capacity of 1.2-1.3 mAh cm⁻² for 80 cycles with 3% FEC. Without FEC additive, the MPC/Se cathode capacity gradually decays from 1.3 mAh cm⁻² to 0.9 mAh cm⁻² in the 50 cycles, and then quickly drops to 0.1 mAh cm^{-2} in the subsequent 20 cycles. The results in Figure 45 suggest that the FEC additive becomes even more critical for Se cathodes with higher Se loadings.



Figure 46. a) Optical images of Na metals, glass fibres, and MPC/Se cathodes and b) EDS analysis of sodium metals, recycled after 200 cycles from Na-Se batteries using EC: DEC electrolytes with or without 3 vol.% FEC.

A detailed comparison between this work and previous studies on Se-based cathode electrodes in carbonate electrolyte is made, in terms of the synthesis process, Se content, and electrochemical performance (Tables 5). Significant progress has been made in Se cathode design; however, they used complex processes and expensive precursors. The MPC synthesis process's simplicity as a Se host material, synthesized by one-step pyrolysis of commercial PVDF, makes it easy to scale up for practical applications. Besides, the current study's Se content (48 wt.%) is also comparable and even higher in some cases with other referred works, showing good and relatively stable capacity.



Figure 47. Schematic illustration of the improvement in the MPC/Se cathode and sodium metal anode using FEC additive in the carbonate electrolytes.

In summary, the excellent performance of MPC/Se cathode in Na-Se batteries could be attributed to the unique structure of MPC and the addition of FEC in the carbonate electrolyte. Microporous carbon prepared from direct pyrolysis of PVDF could effectively confine Se active material and allow fast Na ion and electron transport in the MPC/Se cathode. The FEC additive's use brings benefits to both MPC/Se cathode and Na metal anode, as schematically shown in Figure 47. First, the FEC additive significantly reduced the dissolution of polyselenides into the electrolyte. It suppressed the shuttle effect by forming a robust and stable SEI layer on MPC/Se cathode, thus keeping active Se over long-term cycling. Secondly, the FEC additive induced the formation of a protective SEI layer on the sodium metal surface. The FEC-induced SEI and the

suppressed soluble polyselenides collectively contributed to preserving smooth and compact Na anode, which was found to be a key factor for enabling high-capacity and long-lasting Na-Se batteries with high Se loadings.

MPC/Se cathode has been prepared and employed as a positive electrode in sodiumselenium batteries. The results showed that not the unique structure of microporous carbon can suppress the dissolution of selenium into the electrolyte and increases the cell life and properties, 3% FEC electrolyte additive has also influenced both MPC/Se and sodium metal stability by creating a stable SEI layer on their surface to prohibit selenium and polyselenide dissolution from MPC/Se into the electrolyte and protecting the structural consistency of Na metal anode by reducing the deposition of solid polyselenide deposition.

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Cathode	Synthesis method for porous carbon	Se content (wt%)	Electrolyte	Performance	Ref.
CPAN/Se fibers	Electrospinning of PAN/Se, heat treatment	36	1 M NaClO ₄ , EC-DEC	490 mA h g ⁻¹ at 67.8 mA g ⁻¹	[136]
Se@mesoporous carbon	Soft template and catalyst reaction, carbonization	30	1 M NaClO ₄ , EC-DMC	485 mA h g^{-1} at 169.5 mA g^{-1}	[90]
Se/NPCPs	ZIF-67 carbonization	48.5	1 M NaClO ₄ , EC-DEC, 3% FEC	437.3 mA h g ⁻¹ at 339 mA g ⁻¹	[128]
Se@NHC	Heat treatment of silica spheres containing a solid core and a porous shell	52	1 M NaClO ₄ , EC-DEC	339 mA h g^{-1} at 1356 mA g^{-1}	[167]
CNF/Se composite and C- coated separato	KOH activation of CNF paper	72.1	1 M NaClO ₄ , EC-DMC	599 mA h g^{-1} at 67.8 mA g^{-1}	[70]
Carbon-Selenium composites	annealing PTCDA	54	1 M NaClO ₄ , EC-DMC	595 mA h g ⁻¹ at 50 mA g ⁻¹	[66]
Se@CNFs-CNT	Heat treatment of PAN-CNT fibers	35	1 M NaClO ₄ , EC-DEC	590 mA h g ⁻¹ at 50 mA g ⁻¹	[69]
Se-PAN derived carbon nanofibers	Heat treatment of PCNFs	52	1 M NaClO ₄ , EC-DEC	595 mA h g^{-1} at 100 mA g^{-1}	[82]
Se-CCN	KOH activation of carbon derived cellulose	53	1 M NaClO ₄ , EC-DMC	613 mA h g ⁻¹ at 67.8 mA g ⁻¹	[96]
Se-Carbon with Slit micropores	Calcinations of carbon precursor layer on the CNTs	50.2	1 M NaClO ₄ , propylene carbonate/ ethylene carbonate/	596 mA h g^{-1} at 67.8 mA g^{-1}	[29]
MPC/Se	Carbonization of PVDF	48	1 M NaClO ₄ , EC-DEC, FEC	544 mA h g^{-1} at 67.8 mA g^{-1}	This work

Chapter 6: Nanoscale Al₂O₃ Coating to Stabilize Selenium Cathode for Sodium-Selenium Batteries[§]

This chapter was the extended work of the previous chapter (chapter 5). The cathode surface modification was employed to enhance the battery system's electrochemical properties in chapter 4 for Na/Se batteries. The Na-Se batteries prepared in the previous chapter were promising energy storage systems for grid and transportation applications due to the high volumetric energy density and relatively low cost. However, such Na-Se batteries' development has been hindered by the shuttle effect originating from polyselenide dissolution from the Se cathode. This phenomenon could be significantly suppressed using FEC additive, causing the formation of SEI layer on the cathode, as discussed in the previous chapter. Herein, we reported the utilization of nanoscale Al₂O₃ surface coating by atomic layer deposition (ALD) to protect a microporous carbon/Se (MPC/Se) cathode and reduce polyselenide dissolution, using the optimized electrolyte composition derived from the chapter 5 results. Compared to the pristine MPC/Se, Al₂O₃-coated MPC/Se cathode exhibited improved discharge capacity, cycling stability, and rate capability in Na-Se batteries. Post-cycling analysis disclosed that Al₂O₃ coating on MPC/Se cathode effectively suppressed the polyselenide dissolution, facilitated thin and stable SEI layers, reduced charge transfer resistance, and thus improving the overall performance of Na-Se batteries prepare in chapter 5. This work suggests the effectiveness of interface control by ALD in enabling high-performance Na-Se batteries and might shed light on the development of new-generation Li/Na-chalcogenide batteries.

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Lithium-ion batteries (LIBs) have made a revolution in portable electronic devices over decades. They have been used in electric vehicles, hybrid electric vehicles, and grid energy storage systems due to their long cycle life and high energy density [129]. However, LIBs using intercalation chemistry gradually approaches their theoretical limit and cannot meet the increasing demand for higher energy density and lower cost from end-users in the automotive industry and stationary applications [115]. Therefore, it becomes imperative to develop new-generation battery technologies that satisfy these requirements. Among various potential systems, sodium-selenium (Na-Se) batteries have drawn much attention because of the large abundance and low cost of sodium and decent energy density of Se [73]. As a cathode material, Se provides a moderate gravimetric capacity of 678 mAh g⁻¹, a high volumetric capacity of 3270 mAh cm⁻³, and possesses a high electronic conductivity of 1×10^{-3} S m⁻¹ (*vs.* 5×10^{-28} S m⁻¹ for S) [17, 95, 171]. These advantages of Se have stimulated growing research in developing Li-Se and Na-Se batteries over the past years.

Na–Se batteries are still in their infant stage and face a significant challenge, *i.e.*, shuttle effect caused by polyselenide dissolution from Se cathodes. The shuttle effect leads to the loss of active Se material. It results in Na metal anode corrosion, causing low Coulombic efficiency (CE) and rapid performance decay in Na-Se batteries [17, 95, 171, 172]. To date, several approaches have been developed to address the shuttle effect problem, and the confinement of Se into porous carbon matrix is one of the most promising strategies [30, 66, 82, 90, 96, 125, 173]. For example, Wang and co-workers prepared Se/mesoporous carbon at 600 °C under vacuum. The Se/mesoporous carbon cathode delivered a specific capacity of 340 mAh g⁻¹ after 380 cycles in Na-Se batteries [90].

Moreover, several recent works have explored various metal-organic frameworks (MOF) (such as zinc-glutamate MOF, ZIF-67, and ZIF-8) [126-128] as starting materials to synthesize porous carbon as hosts for Se cathodes in Na-Se batteries. Although the space confinement has been effective in improving the Se cathode's overall performance, polyselenide dissolution still occurs in Na-Se batteries using porous carbon confined Se cathode. In general, Na-Se batteries show a more severe shuttle effect than their Li-Se counterparts [171]. One main reason could be due to the larger ionic radius of Na⁺ (102 pm) than Li⁺ (74 pm), which might cause more considerable volume change in the Se cathode and alter reaction pathways of Se in Na-based batteries [29, 159]. Goodenough et al. [29] found that during the first discharge process, Se in microporous carbon underwent step-wise reduction to Na₂Se, with the formation of soluble intermediate polyselenides (Na₂Se_x) in Na-Se batteries. Therefore, it is necessary to develop and use multiple strategies to stabilize Se cathode for high-performance Na-Se batteries. The Se into the electrolyte's dissolution could increase the possibility of the multi-step transformation of Se to Na₂Se rather than one single step reaction. Also, the electrolyte is another essential factor that contributes to this phenomenon. For Li-Se batteries having carbonate-based electrolytes, Se undergoes a one-step reaction from Se to Li₂Se, without forming unstable polyselenide intermediates, and is featured with one single plateau in its charge-discharge curves [17, 82].

In addition to the space confinement strategy, the surface coating has also been explored as a practical approach to address the shuttle effect problem in S-based [174-177] and Se-based batteries [104, 178]. Ideally, the surface coating layer should be thin and uniform to reduce intermediate products' dissolution while allowing fast Li-ion and electron diffusion. In recent years, atomic layer deposition (ALD) has emerged as a powerful technique to realize uniform surface coatings on the anode and cathode for Li-ion batteries [121-123] and next-generation batteries (such as Na-ion, Li-S) [124, 179], to prevent unwanted interfacial reactions and improve the overall performance of batteries. Compared to other coating techniques, ALD provides precise control over thin films' thickness at the nanoscale level and excellent uniformity on even high-aspect-ratio substrates [112, 180], promising it great potential for surface and interface engineering in various battery systems. However, the prospect of ALD for interface design in Na-Se batteries is yet to be fully exploited.

Herein, we reported the utilization of nanoscale Al₂O₃ surface coating by ALD to stabilize the Se cathode for high-performance Na-Se batteries with carbonate-based electrolytes. Microporous carbon (MPC) prepared by pyrolysis of polyvinylidene fluoride (PVDF) was adopted to fabricate MPC/Se cathode. It was found that Al₂O₃ surface coating effectively suppressed the polyselenide dissolution from the MPC/Se cathode, thus reducing the loss of Se active material and improving the overall performance of Na-Se batteries.

6.1.1 Preparation of MPC, MPC/Se, and MPC/Se-Al₂O₃

Poly (vinylidene fluoride) ((-CH₂CF₂-)_n, MW: 64.035 g mol⁻¹, Alfa Aesar) was put in a tube furnace (Lindberg/Blue M Mini-MiteTM) and heated up to the temperature of 800 °C with a heating rate of 10 °C min⁻¹ and kept for 1h under the inert gas environment (nitrogen 99.999%) to perform the pyrolysis. Black products collected after pyrolysis were microporous carbon, and no further activation on MPC was required. The MPC/Se composite was prepared by a melting diffusion method. Briefly, in a mortar, sublimed selenium powder, -100 mesh (99.5%, Sigma Aldrich) and MPC with the same weight ratio of 50:50 were mixed for 1h and sealed a 50 mL stainless steel autoclave. This process was conducted in a glovebox workstation under the argon atmosphere's protection with H₂O and O₂ levels below 0.1 ppm. The autoclave was put into a furnace followed by heat treatment at 260 °C for 12 h. The melting diffusion method used the

capillary force to diffuse Se into microspores of MPC. To obtain the cathode electrode, 80 wt% of MPC/Se composite, 10 wt% of carbon black (MTI Co.), and 10 wt% of sodium alginate (Ward's Science Co., Ltd., 0.5 wt% aqueous solution) were mixed in planetary mortar to form a uniform slurry, which was then pasted on an Al foil current collector by using a doctor blade. The electrode was kept at room temperature (RT) overnight for initial water evaporation and then underwent complete drying in a vacuum oven at 60 °C for 12 h. Subsequently, the electrode was cut into round disks with a diameter of 12.7 mm for coin-cell assembly.

The coating of Al_2O_3 on MPC/Se electrode was performed at 100 °C by supplying trimethylamine (TMA) and H_2O into a commercial ALD reactor (GEMStarTM XT Atomic Layer Deposition Systems, Arradiance, USA). The thickness of Al_2O_3 on MPC/Se cathode was adjusted using 10 and 20 ALD cycles, and the prepared sample was designated as MPC/Se- $10Al_2O_3$ and MPC/Se- $20Al_2O_3$ respectively.

6.1.2 Structural and electrochemical characterizations of MPC and MPC/Se composites

A scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) (Tescan MIRA3) was used to examine the morphology and structure of different samples. The electrochemical properties of the MPC/Se composites were evaluated in CR 2032 coin cells by using Na foil as the counter electrode. The assembly of coin cells was performed in a glovebox workstation with argon-protecting gas (99.999%). Each coin cell was composed of one MPC/Se electrode as the cathode, Na metal as the anode, and glass fibre as the separator. The electrolyte was 1M NaClO₄ in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 v/v) with 3 vol.% fluoroethylene carbonate (FEC) additive. The cycling performance of the coin cells was tested in a voltage window of 0.5 to 3 V on a Neware BTS 4000 battery testing system.

6.2 Results and Discussion



Figure 48. (a) HRTEM image of MPC; (b) SEM image of MPC/Se; (c) Raman spectra of MPC and MPC/Se; (d, e) SEM images and (f) EDX elemental mapping of MPC/Se coated with 10-ALD cycle Al₂O₃ (MPC/Se-10Al₂O₃); (g) schematic illustration of the preparation process for MPC/Se-Al₂O₃

MPC was synthesized by the direct pyrolysis of poly(vinylidene fluoride) at 800 °C in a nitrogen environment and used as the Se host without any further activation process. Previous work has shown that MPC prepared at this condition exhibited the highest surface area and dominant microporous feature, significant merits for confining Se in the cathode [141, 142, 162]. High-resolution transmission electron microscopy (HRTEM) characterization discloses the disordered structure of the as-synthesized MPC (Figure 49a). After the Se impregnation, MPC/Se 120

composite displays irregular shapes with particle sizes of about 10-200 µm (Figure 49b). Raman spectra of MPC and MPC/Se (Figure 49c) show two vibration peaks at about 1350 cm⁻¹ and 1600 cm⁻¹, which are assigned to the D band (disordered carbon originating from sp³ carbons) and G band (hexagonal carbon), respectively [88, 89]. It should be noted that MPC/Se composite displays no apparent peaks in the range of $200 \text{ cm}^{-1} - 500 \text{ cm}^{-1}$, the region for crystalline bulk Se [62]. Raman analysis reveals no bulk Se in the MPC/Se composite, and all Se is mainly encapsulated in the micropores of MPC. Se content in MPC/Se composite was determined to be 48 wt% by thermogravimetric analysis. Al₂O₃ coating was deposited on the MPC/Se electrode by ALD using 10 cycles and 20 cycles, and the prepared samples were designated as MPC/Se-10Al₂O₃ and MPC/Se-20Al₂O₃ respectively. As seen in Figures 49d and 49e, MPC/Se-10Al₂O₃ turns slightly darker in the SEM due to the non-conductive nature of Al₂O₃ coating and retains its morphology MPC/Se. Elemental mapping by energy-dispersive X-ray spectroscopy (EDX) in Figure 49f shows the uniform distribution of Al and O elements on the MPC/Se cathode's surface. The thickness of Al₂O₃ on MPC/Se-10Al₂O₃ and MPC/Se-20Al₂O₃ is about 1 nm and 2 nm, respectively, based on the growth rate of Al₂O₃ on standard Si wafers [112, 180]. The preparation process for MPC/Se-Al₂O₃ is illustrated in Figure 49g.



Figure 49. (a) Cycling performance of MPC/Se, MPC/Se- $10Al_2O_3$, and MPC/Se $-20Al_2O_3$ measured at 0.1C (1C = 678 mA g⁻¹); charge-discharge profiles of MPC/Se and MPC/Se $-10Al_2O_3$ in the (b) 1st cycle, (c) 50th cycle, and (d) 100th cycle; (e) rate capability of MPC/Se and MPC/Se $-10Al_2O_3$; (f) cycling stability of MPC/Se $-10Al_2O_3$ tested at 0.1C in the first 10 cycles and 0.5C afterward.

The influence of Al_2O_3 coating on the MPC/Se cathode's electrochemical performance is studied in Na-Se batteries between 0.5V and 3V at 0.1C, and the results are shown in Figure 50. As shown in Figure 50a, MPC/Se-10Al₂O₃ and MPC/Se-20Al₂O₃ exhibit an initial capacity of about 1050 mAh g⁻¹, similar to the pristine MPC/Se. After the 1st cycle, however, there is a dramatic difference in the specific capacity for the MPC/Se cathodes with and without Al_2O_3 coating. The discharge capacity in the 2^{nd} cycle was 534 mAh g⁻¹, 664 mAh g⁻¹, and 639 mAh g⁻¹ for MPC/Se, MPC/Se-10Al₂O₃, and MPC/Se-20Al₂O₃, respectively. The capacity drop from the 1^{st} cycle to the 2^{nd} one in all the three samples could be ascribed to SEI film formation and the decomposition of electrolytes on the MPC/Se cathode [90]. For MPC/Se cathode, the capacity decreases gradually from 534 mAh g⁻¹ in the 2^{nd} cycle to 446 mAh g⁻¹ after 80 cycles, and then undergoes rapid decay to 396 mAh g⁻¹ until 100 cycles. In contrast, MPC/Se-10Al₂O₃ could still deliver a specific capacity of 570 mAh g⁻¹ after 100 cycles. The MPC/Se cathode's capacity retention from the 2^{nd} cycle to the 100^{0h} cycle was elevated from 73% to 86% by using Al₂O₃ coating. Moreover, MPC/Se-20Al₂O₃ exhibits a specific capacity and cycling performance lower than MPC/Se-10Al₂O₃ but better than the new MPC/Se cathode. Further increase of Al₂O₃ coating more than 20 cycles causes an obvious decrease in the specific capacity. The reason could be due to the insulating nature of Al₂O₃ coating, which might slow down Li ions' diffusion through the SEI layer. [121-124]. This result suggests the importance of Al₂O₃ coating thickness for achieving optimal protection effect in Se cathodes.

Figure 50b-50d presents charge/discharge curves of the MPC/Se and MPC/Se- $10Al_2O_3$ in the 1st, 50th, and 100th cycle tested at 0.1C. As shown in Figure 50b, both MPC/Se and MPC/Se- $10Al_2O_3$ exhibit one obvious plateau during the discharge and charge process, which are characteristic of micropore-confined Se [90, 125-128]. Coulombic efficiency in the 1st cycle is calculated to be 51.4% and 60.9% for MPC/Se and MPC/Se- $10Al_2O_3$, respectively, implying that Al_2O_3 coating reduces the side reaction between the Se electrode and the electrolyte. Moreover, it is found from Figure 50b-50d that Al_2O_3 coating also minimizes the polarization of MPC/Se cathode during the discharge and charge process. For example, midpoint-voltage differences in the 50th and 100th cycles are 0.30 V and 0.46V for MPC/Se, while 0.22V and 0.24V for MPC/Se-

 $10Al_2O_3$ (Figure 50c and 50d), indicating enhanced reaction kinetics of MPC/Se by Al_2O_3 coating. The improved capacity and kinetics in MPC/Se- $10Al_2O_3$ could result from the protective effect of nanoscale Al_2O_3 coating, which alleviates polyselenide dissolution and reduces the deposit of solid polyselenides. Moreover, a previous study in Na-ion batteries has shown that the Al_2O_3 coating on the electrode might convert to a stable Na-Al-O layer, which served as a Na buffer layer to facilitate Li-ion diffusion [181, 182]. As a result of the improved kinetics, the MPC/Se- $10Al_2O_3$ could deliver a specific capacity of 544.4 mAh g⁻¹, 518.5 mAh g⁻¹, 458.3 mAh g⁻¹, 422.5 mAh g⁻¹, and 343.8 mAh g⁻¹ at 0.1C, 0.2C, 0.5C, 1C, and 2C, respectively, while MPC/Se shows a specific capacity of 477.7 mAh g⁻¹, 463.3 mAh g⁻¹, 370.1 mAh g⁻¹, 353.3 mAh g⁻¹, and 245.7 mAh g⁻¹ under the same condition. At last, the cycling test at 0.5C shows that MPC/Se- $10Al_2O_3$ can maintain a specific capacity of 320 mAh g⁻¹ after 100 cycles (Figure 50f). From the results in Figure 50, it can be concluded that ALD Al_2O_3 coating effectively improves the specific capacity, cycling stability, and rate capability of the MPC/Se cathode in Na-Se batteries.



Figure 50. Nyquist profiles of MPC/Se and MPC/Se-10Al₂O₃ (a) before cycling and (b) after 100 cycles (Insert shows the equivalent circuit used to fit the Nyquist plots).

Table 6. EIS parameters obtained by fitting the Nyquist plots of MPC/Se and MPC/Se-10Al₂O₃ after 100 cycles.

Sample after cycling	$\mathbf{R}_{s}\left(\Omega\right)$	$\mathbf{R}_{\mathrm{SEI}}(\Omega)$	$\mathbf{R}_{\mathrm{CT}}(\Omega)$
MPC/Se	6.7	40.9	90.6
MPC/Se-10Al ₂ O ₃	8.4	20.2	68.6

To find out the underlying mechanism for performance improvement by ALD Al₂O₃ coating, electrochemical impedance spectroscopy (EIS) measurement was performed on MPC/Se and MPC/Se-10Al₂O₃ before and after 100 cycles, and the results are presented in Figure 51. As seen in Figure 51a, both MPC/Se and MPC/Se-10Al₂O₃ display one semicircle in the highfrequency region, which corresponds to the charge transfer resistance (R_{CT}) at the electrodeelectrolyte interface, and one inclined line in the low-frequency region, which is interpreted as the finite length Warburg impedance [91]. The smaller R_{CT} in MPC/Se-10Al₂O₃ might be due to the improved physical contact between the electrode material and Al current collector by ultrathin Al₂O₃ coating directly on the electrode, which allows faster electron diffusion [183]. The Nyquist profiles of MPC/Se and MPC/Se-10Al₂O₃ after cycling present one semicircle (R_{CT}) in the high-frequency region, Warburg impedance in the low-frequency domain, and another semicircle in the medium-frequency region, which can be assigned to the Li-ion diffusion resistance at the SEI (R_{SEI}) [91]. The Nyquist profiles are fitted using the equivalent circuit inserted in Figure 51b to obtain EIS parameters for MPC/Se and MPC/Se-10Al₂O₃ (Table 6). From Table 6, it is evident that R_{SEI} reduces from 40.9 Ω to 20.2 Ω , while R_{CT} decreases from 90.6 Ω to 68.6 Ω for the MPC/Se cathode with Al₂O₃ coating. EIS analysis clearly indicates that Al₂O₃ surface coating positively affects the formation of SEI layers and reduce charge transfer and Li-ion diffusion resistances on the MPC/Se cathode.



Figure 51. SEM images of (a, b, c) MPC/Se electrode, and (d, e, f) MPC/Se-10Al₂O₃ electrode after 100 cycles.

The morphologies of MPC/Se and MPC/Se-10Al₂O₃ after 100 cycles are examined, and the typical SEM images are depicted in Figure 52. From Figure 52a-52c, it can be found that the cycled MPC/Se electrode is covered with thick SEI layers and has much less porosity than the uncycled one. The thick SEI layers could originate from the decomposition of electrolytes and the deposit of solid polyselenides (Na₂Se and Na₂Se₂) on the MPC/Se surface due to the shuttle effect. In contrast, the cycled MPC/Se-10Al₂O₃ cathode possesses much thinner SEI layers. As a result, the sharp edges in the MPC/Se particles are still visible (Figure 52f) compared to those before battery cycling (Figure 52e). EIS and post-cycling analysis suggest that nanoscale Al₂O₃ surface coating facilitates robust and thin SEI layers on the MPC/Se electrode, which are believed to account for the reduced charge transfer resistance and Li-ion diffusion resistance at the electrode-electrolyte interface.



Figure 52. SEM images of glass fibers recycled after 100 cycles from (a, b) the MPC/Se cell, and (c, d) the MPC/Se-10Al₂O₃ cell. (Insert in (b) shows the EDX spectrum on the solid particles).

Glass fibres recovered from cycled MPC/Se and MPC/Se-10Al₂O₃ cells are further examined to understand the polyselenide dissolution. The typical SEM pictures have shown that glass fibre facing the MPC/Se electrode is deposited with microsized solid particles. EDX analysis confirms strong signals from Na and Se elements, implying that the solid particles might be Na₂Se and Na₂Se₂. In contrast, glass fibre from the MPC/Se-10Al₂O₃ cell retains its original fibrous structure and shows no prominent large solid deposits. This figure provides additional evidence for the suppressed polyselenide dissolution from the MPC/Se cathode by Al₂O₃ surface coating.

ALD nanoscale Al₂O₃ surface coating was successfully applied to solve polyselenide dissolution problem and enable microporous carbon/Se (MPC/Se) cathode for stable and high-

capacity Na-Se batteries. The thickness of the Al₂O₃ coating had a profound influence on the MPC/Se cathode's overall performance. The MPC/Se cathode's optimal electrochemical performance was achieved by using 10 ALD cycles of Al₂O₃ coating. Al₂O₃ coated MPC/Se cathode exhibited a reversible discharge capacity of 664 mAh g^{-1} in the 2nd cycle and 570 mAh g^{-1} after 100 cycles. Moreover, Al₂O₃ coating on MPC/Se cathode also improved the rate capability and reduced the polarization during charge/discharge processes. The enhanced performance was due to that nanoscale Al₂O₃ coating suppressed the dissolution of polyselenides, induced the formation of stable and thin SEI layers, and thus decreased the charge transfer resistance at the electrode-electrolyte interface.

Chapter 7: Conclusions and perspectives

7.1 Conclusions

A series of experiments were conducted in this thesis to synthesize various carbon hosts for confining selenium to be used as a cathode material for Li/Na-Se batteries. The electrodeelectrolyte interface was also modified, and different parameters were investigated to do this in terms of electrolyte additive and electrode surface coating. The importance of metal anode was also highlighted for future works in this field. This thesis covered topics of material synthesis, underlying mechanisms, interfacial behaviours, and electrochemical performances.

In the first step, preparation of carbon host was focused, and the correlation between carbon structure and battery performance was investigated. Zeolitic imidazolate framework-8 (ZIF-8), a subclass of MOFs, as the microporous carbon source was used, and the Li-Se batteries' electrochemical performances were studied. To improve the electrode efficiency, Alucone coating was applied on the electrode, and their performance was studied. Results showed that the other types of carbon host are needed for higher selenium loadings, and the issues at the electrode/electrolyte interface should be solved. This fixing can be attributed to the two sections of electrode modification and electrolyte optimization addressing the polyselenide dissolution problem. These both have been investigated in the following chapters.

In the next chapter, carbon derived from polyvinylidene fluoride (PVDF) was used as a selenium host for high-performance lithium-selenium (Li-Se) batteries. The optimized carbon with regulated selenium content and loading showed a promising result by delivering the reversible capacity of 508.8 mAh g^{-1} at 0.1C after 100 cycles. The results showed that micropores in MPC were the determinant factor for affecting MPC/Se composites' performance. The exceptional cyclability of MPC/Se cathodes was mainly due to the uniform distribution of

Se in micropores, which could alleviate side reactions with electrolytes and prevent the dissolution of polyselenides in carbonate electrolytes.

The following chapter describes the electrode/electrolyte interfacial design in terms of electrolyte optimization. The FEC electrolyte additive was used, and their content was optimized in Na-Se batteries. 3% vol. FEC additive significantly reduced the dissolution of polyselenides into the electrolyte. It suppressed the shuttle effect by forming a robust and stable SEI layer on MPC/Se cathode, thus keeping active Se over long-term cycling. The MPC/Se cathode with a 3% FEC additive maintained a specific capacity of 382 in the 100th cycle. The effectiveness of FEC additive on the prevention of Na metal corrosion from soluble polyselenides, and preserving the structural integrity of Na anode was also confirmed.

The last chapter was the design of the electrode/electrolyte interface at the electrode side. The nanoscale Al_2O_3 surface coating was applied to the MPC/Se cathode by the atomic layer deposition technique. 10 ALD cycles of Al_2O_3 coated MPC/Se cathode exhibited a reversible discharge capacity of 570 mAh g⁻¹ after 100 cycles in Na-Se batteries. The enhanced performance was due to that nanoscale Al_2O_3 coating suppressed the dissolution of polyselenides, induced the formation of stable and thin SEI layers, and thus decreased the charge transfer resistance at the electrode-electrolyte interface.

7.2 Contributions

I made several contributions throughout my Ph.D. career that help this field of study. These contributions will make a pathway for reviewers to have a general and detailed understanding of the concepts that were investigated:

• We have developed a facile activation-free approach to make high conductive carbon with enough micropores to confine Se and used it in scalable, practical applications of

Li/Na-Se batteries.

- Addressed the polyselenides dissolution and preserving the structural integrity of Na anode by introducing FEC-induced SEI, contributing to the enhanced cycling stability and specific capacity of Na-Se batteries
- Utilized nanoscale Al₂O₃ surface coating on MPC/Se cathode to reduce charge transfer resistance and improve discharge capacity, cycling, and rate capability in Na-Se batteries

7.3 Perspectives

Despite advancements made in this thesis, further research and breakthrough need to obtain high-performance materials for Li/Na-Se batteries. Some suggestions are provided in the following part.

1. Carbon matrix is one of the most critical factors that can affect the battery cell's electrochemical performance. In current researches, the loading of active material into the carbon host is not too high or needs a complex synthesis method. This thesis aimed for the highly porous carbon host with desirable surface area, conductivity, and micro/meso pore sizes while maintaining the facile sample preparation. Further works should emphasize the simplicity of carbon preparation to confine higher loadings of the active metal.

2. Confinig selenium into the carbon host is another exciting part of the composite preparation that needs further investigation. Researches in this field are barely studying the effect of the confining method on the battery's electrochemical behaviour. Melt diffusion, doping/chemical bonding, and active metal incorporation are some of the most favourable pathways to load the active metal into the carbon matrix. Further studies are needed to find the primary methods for increasing the dynamic metal-substrate interaction and reducing the potential of polyselenide dissolution into the electrolyte.

3. Metal anode should be explored more to provide a stable reaction mechanism over

cycles. Several parameters are involved in Li/Na metal structural integrity, requiring more experimental and computational investigation. Thus reaching the higher energy density is more practical.

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- Mohammad Hossein Aboonasr Shiraz, Hongzheng Zhu, Yulong Liu, Xueliang Sun, Jian Liu. "Activation-free synthesis of microporous carbon from polyvinylidene fluoride as host materials for lithium-selenium batteries", Journal of Power Sources, (2019)
- Mohammad Hossein Aboonasr Shiraz, Peter Zhao, Jian Liu. "High-Performance Sodium-Selenium Batteries Enabled by Microporous Carbon/Selenium Cathode and Fluoroethylene Carbonate Electrolyte Additive", Journal of Power Sources, (2020)
- Mohammad Hossein Aboonasr Shiraz, Hongzheng Zhu Jian Liu. "Nanoscale Al₂O₃ Coating to Stabilize Selenium Cathode for Sodium-Selenium Batteries", Journal of Materials Research, (2019)

(B) Conference Proceeding Journal Papers (First Author)

 Mohammad Hossein Aboonasr Shiraz, Yuhai Hu, Jian Liu. "A Stable Lithium-ion Selenium Batteries Enabled by Micropororous Carbon/Se and Fluoroethylene Carbonate Additive", ECS Transactions, (2020)

(C) Peer-reviewed Journal Papers Related to the Ph.D. Study Duration (First and Co-author)

- Peter Zhao, <u>Mohammad Hossein Aboonasr Shiraz (co-first author)</u>, Hongzheng Zhu, Yihao Liu, Li Tao, Jian Liu. "Hierarchically porous carbon from waste coffee grounds for high-performance Li-Se batteries", Electrochimica Acta (2019)
- Hongzheng Zhu, <u>Mohammad Hossein Aboonasr Shiraz</u>, Lu Yao, Keegan Adair, Zhiqiang Wang, Huan Tong, Xueyang Song, Tsun-Kong Sham, Mohammad Arjmand, Xiping Song, Jian Liu. "Iron beta-diiminate complexes with As-2-, As-4-and As-8ligands", Chemical Communications (2020)
- 7. Hongzheng Zhu, <u>Mohammad Hossein Aboonasr Shiraz</u>, Liang Liu, Yuhai Hu, Jian Liu.
 "Facile and low-cost Al₂O₃ coating as an artificial solid electrolyte interphase layer

on graphite/silicon composites for lithium-ion batteries", Nanotechnology (2020)

- Yue Zhang, Wei Lu, Peter Zhao, <u>Mohammad Hossein Aboonasr Shiraz</u>, Dan Manaig, Donald J. Freschi, Yulong Liu, Jian Liu. "A Durable Lithium-Tellurium Battery: Effects of Carbon Pore Structure and Tellurium Content", Carbon (2020)
- 9. Hongzheng Zhu, <u>Mohammad Hossein Aboonasr Shiraz</u>, Lu Yao, Keegan Adair, Zhiqiang Wang, Huan Tong, Xueyang Song, Tsun-Kong Sham, Mohammad Arjmand, Xiping Song, Jian Liu. "Molecular-Layer-Deposited Tincone: a New Hybrid Organic-Inorganic Anode Material for Three-Dimensional Microbatteries", Chemical Communications (2020)
- Jian Liu, Hongzheng Zhu and Mohammad H. A. Shiraz. "Toward 3D Solid-State Batteries via Atomic Layer Deposition Approach", Frontiers in Energy Research, (2018)
- (D) Papers Submitted or in Progress
 - Xueyang Song, Huibing He, <u>Mohammad Hossein Aboonasr Shiraz</u>, Hongzheng Zhu, Ali Khosrozadeh, Jian Liu. "Enhanced Reversibility and Electrochemical Window of Zn-ion Batteries with Acetonitrile/Water-in-Salt Electrolytes", Submitted Chemical Communications (2020)
 - 12. <u>Mohammad Hossein Aboonasr Shiraz,</u> Jian Liu. "Comprehensive Insights into the Design Strategies and Research Progress of Carbonate Based Electrolytes in Li/Na for Selenium and Selenium Sulfide Rechargeable Batteries", In Progress
 - Mohammad Hossein Aboonasr Shiraz, Jian Liu. "Durable Lithium/Selenium Batteries by Eliminating Polyselenides Dissolution via the Integration of MOF-Derived Microporous Carbon and Molecular Layer Deposited Coating", In Progress
- (E) Previous Publications
 - 14. <u>Mohammad Hossein Aboonasr Shiraz</u>, Mehran Rezaei, Fereshteh Meshkani. **''Microemulsion synthesis method for preparation of mesoporous nanocrystalline** γ -Al₂O₃ powders as catalyst carrier for nickel catalyst in dry reforming reaction'', International Journal of Hydrogen Energy, (2016)

- 15. <u>Mohammad Hossein Aboonasr Shiraz</u>, Mehran Rezaei, Fereshteh Meshkani. "**Ni** catalysts supported on nano-crystalline aluminum oxide prepared by a microemulsion method for dry reforming reaction", Research on Chemical Intermediates, (2016)
- 16. <u>Mohammad Hossein Aboonasr Shiraz</u>, Mehran Rezaei, Fereshteh Meshkani. "Preparation of nanocrystalline Ni/Al₂O₃ catalysts with the microemulsion method for dry reforming of methane", The Canadian Journal of Chemical Engineering, (2016)
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- Fereshteh Meshkani, Mehran Rezaei, <u>Mohammad Hossein Aboonasr Shiraz</u>.
 "Preparation of High Temperature Water Gas Shift Catalyst with Coprecipitation Method in Microemulsion System", Chemical Engineering Research and Design , (2016)
- (F) Conference papers
 - 19. Mohammad Hossein Aboonasr Shiraz, Hongzheng Zhu, Jian Liu. "Electrode and Interface Design for High-Performance Lithium/Sodium-Selenium Batteries", Pacific Rim Meeting on Electrochemical & Solid state Science (PRiME 2020)
 - 20. Hongzheng Zhu, <u>Mohammad Hossein Aboonasr Shiraz</u>, Jian Liu. "Tincone-New Hybrid Organic-Inorganic Anode Material for High Performance Li-Ion Battery", Pacific Rim Meeting on Electrochemical & Solid state Science (PRiME 2020)
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 - 23. <u>Mohammad Hossein Aboonasr Shiraz</u>, Mehran Rezaei, Fereshteh Meshkani, Nima Bayat. "**Preparation of nanocrystalline gamma alumina with high surface area by** 147

microemulsion method and its application as catalyst support in dry reforming reaction", 2nd International Conference on Nano Technology- ICN2014.

24. Nima Bayat, Mehran Rezaei, Fereshteh Meshkani, <u>Mohammad Hossein Aboonasr Shiraz</u> **''Thermodynamic decomposition of methane to CO**_X free hydrogen over Ni catalysts support on nanocrystaline gamma Al₂O₃'', 2nd International Conference on Nano Technology- ICN2014.