LIGNIN-DERIVED HARD CARBON ANODE FOR POTASSIUM-ION BATTERIES: INTERPLAY AMONG LIGNIN MOLECULAR WEIGHT, MATERIAL STRUCTURES, ELECTROLYTE CHEMISTRY, AND STORAGE MECHANISMS

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Abstract

Potassium-ion battery (PIB) is a rising star in the rechargeable battery field due to its potential low cost and high energy for large-scale applications. Hard carbon (HC) is one of the most popular anodes for practical PIBs due to its high K-ion storage and relatively low material cost. Primarily, biomass (such as lignin) represents an abundant source for synthesizing HC. This thesis developed a series of HCs from lignin with different molecular weights (MWs) at serial pyrolysis temperatures (PTs) of 500-1000 °C, exhibiting varying electrochemical performance. The best lignin-derived HC (LHC) was pyrolyzed from medium-MW lignin at 700 °C (M700) and delivered a high reversible specific capacity of ~300 mAh g⁻¹ at 50 mA g⁻¹. M700 exhibited an optimal mixture of graphite-like nanocrystals with the most significant interlayer distance and amorphous structure to maximize K-ion storage from bulk insertion and surface adsorption. The role of electrolytes was then investigated to determine the LHC performance and K-ion storage mechanism. We systematically studied the influence of four electrolyte systems, *i.e.*, two K salts $(KPF_6 \text{ and } KFSI)$ in carbonate ester and ether solvents, on ionic mobility, cycling stability, and charge transfer kinetics of M700 in PIBs. It is found that the M700 anode achieved the best cycling stability and kinetics performance in the KFSI EC/DEC electrolyte. Mechanimsic study disclosed that the improved performance could be ascribed to the formation of robust KF-rich SEI resulting from FSI⁻ decomposition, which effectively prevented irreversible side reactions and severe structural decay (e.g., exfoliation and pulverization). The degradation mechanisms of other electrolyte systems are also explained by SEI formation and solvation/desolvation effect. It is expected that this work will provide guidance on the anode and electrolyte selection and design for PIBs in the near future.

Keywords: lignin, hard carbon, potassium-ion batteries, molecular weight, electrolyte, solidelectrolyte interphase, ionic storage mechanism.

Lay Summary

Potassium-ion batteries are emerging energy storage technology with low cost and high energy for large-scale applications. Because traditional graphite anode cannot provide enough space for K-ion storage, a series of hard carbons from lignin was prepared *via* pyrolysis and tried to use as the anodes in potassium-ion batteries. Hard carbon is a popular anode material for practical battery applications due to its good ionic storage capacity and relatively low cost. In order to screen out the best synthesis conditions, three lignin samples with different molecular weights were selected and were set up with serial pyrolysis temperatures. As a result, the hard carbon prepared from lignin with medium molecular weight at 700 °C showed the best electrochemical performance. Furthermore, to understand electrolyte chemistry impacts on hard carbon anode stability and magnify overall battery performance, selected four common electrolytes were selected to optimize the battery system further investigate their compatibility with lignin-derived hard carbon anodes. KFSI in EC/DEC became the most suitable electrolyte system and can stabilize the hard carbon anode by forming effective protection layers on the anode side. To summarize, this work provided a practical application strategy for lignin in the energy storage field and maximize the performance by electrolyte chemistry.

Preface

Chapter 1.1 is a slightly modified version of our published work and has been reproduced here with the permission of the copyright holder. [Zhenrui Wu]., J. Zou, S. Chen, X. Niu, J. Liu, and L. Wang (2021) Potassium-ion battery cathodes: Past, present, and prospects. Journal of Power Sources 484: 229307. Dr. L. Wang and I conceived the idea and designed the review plan. I designed the scientific figures and wrote the manuscript with Dr. J. Liu and Dr. L. Wang, who oversighted the whole project for the research execution and heavily contributed to discussion and revision. All of the authors contributed to the proofreading and discussion of this article.

A version of chapter 1.2, chapter 3, and chapter 5.1 has been under review of Chemical Engineering Journal. [Zhenrui Wu], J. Zou, Y. Zhang, X. Lin, D. Fry, and J. Liu (2021) Ligninderived hard carbon anode for potassium-ion batteries: Interplay among lignin molecular weight, material structures, and storage mechanisms. J. Liu and I conceived the idea, designed the research plan, and wrote the manuscript. I performed the synthesis, conducted the electrochemical testing, and designed scientific figures. J. Zou. provided help in GITT data analysis and result discussion. Y. Zhang contributed to the SEM tests. X. Lin contributed to the Raman tests. D. Fry provided lignin samples with different molecular weights. J. Liu oversighted the whole project for the research activity planning and execution. The authors would like to thank Dr. Mohammad Arjmand and Negin Jalili in the School of Engineering at UBC for their kind help on TGA analysis. The authors are grateful for Dr. Xiping Song and Huan Tong in the State Key Laboratory for Advanced Metals and Materials at the University of Science and Technology Beijing to assist HRTEM characterization.

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electrochemical and characterization results, prepared the scientific figures, and wrote the manuscript. Dr. J. Liu oversight the whole project for the research planning and execution. The authors would like to thank Dr. Michael C.P. Wang in 4D Labs at Simon Fraser University for the help on XPS characterization. The authors are grateful to Dr. Carmen Andrei in Canadian Centre for Electron Microscopy at McMaster University to assist HRTEM characterization.

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Nomenclature

Roman Symbols

b-value	0.5 < b-value < 1, a measure of ionic kinetics
C'	Constant in nanocrystal size calculation, in Å-1
D ⁺	Diffusion co-efficiency, a measure of ionic kinetics, in cm ² s ⁻¹
E ⁰	Theoretical electrode potential, in V
Ea	Activation barrier energy, in kJ mol ⁻¹
Er	Potential change in the decomposition process in duration time, in V
Ι	Intensities of D and G peaks in Raman spectra
İ _(p)	Peak current in CV profiles
k, a, b	Adjustable constants in kinetics calculation
L	The thickness of the electrodes, in cm
La	The cluster size of the nanocrystals
ΜB	Mass of active materials, in gram
M _B	The molecular weight of carbon, in g mol ⁻¹
mol.%	Percentage by molar, a measure of concentration
ppm	Parts per million, a measure of concentration
Q	Total ionic storage capacity in Coulomb
Q _b	Ionic storage capacity via bulk-insertion
Qs	Ionic storage capacity via surface-adsorption
R	The total resistance of batteries in Ohm
R _{ct}	Charge transfer resistance in Ohm
R _f	SEI resistance in Ohm

Rs	Internal Ohm resistance in Ohm
S	The effective area of the electrode, in cm ²
т	Reaction temperature, in °C
t	Reaction time, in hours or minutes
v	Scan rate in RSCV tests, in mV s ⁻¹
V _M	Molar volume of carbon, in cm ³ mol ⁻¹
vol.%	Percentage by volume, a measure of concentration
wt.%	Percentage by mass, a measure of concentration

Greek Symbols

Τ	Duration time in GITT tests, in second
∆Es	Potential change after every equilibrium process, in V
20	The angle between the incident beam and detector in XRD tests
λ	The wavelength of the target material (Cu, Fe, Mo, Cr) in the X-ray tube
σ+	The ionic conductivity in mS cm ⁻¹

Abbreviations

BE	Binding energy, in eV
BET	Brunauer-Emmett-Teller method
C/D	Charging/discharging, a battery test method
CE	Coulombic efficiency, a technical parameter of battery testing
CEI	Cathode-electrolyte interphase
CV	Cyclic voltammetry, a battery test method

DEC	Diethyl carbonate, an organic solvent in the electrolyte
DFT	Density functional theory, a simulation/calculation method
DME	Dimethoxyethane, an organic solvent in the electrolyte
EC	Ethylene carbonate, an organic solvent in the electrolyte
EDX	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ESSs	Energy storage systems
EVs	Electric vehicles
GITT	Galvanostatic intermittent titration technique, a battery test method
HAADF	High-angle annular dark-field
HC	Hard carbon, an anode material for batteries
HEVs	Hybrid electric vehicles
НОМО	Highest occupied molecular orbital
HRTEM	High-resolution transmission electron microscope
KF	Potassium fluoride, a major content in some SEI chemistries
KFSI	Potassium bis(fluorosulfonyl)imide, KN(SO ₂ F) ₂ , a K-salt
КОН	Potassium hydroxide, an activation agent for carbon materials
KPF ₆	Potassium hexafluorophosphate, a K-salt
KTFSI	Potassium bis(trifluoromethanesulfonyl)imide, $KN(SO_2CF_3)_2$, a K-salt
LHC	Lignin-derived hard carbon
LIBs	Lithium-ion batteries
LiPF ₆	Lithium hexafluorophosphate, a Li-salt
LUMO	Lowest unoccupied molecular orbital
MW	Molecular weight, in g mol ⁻¹

NMP	N-methyl-2-pyrrolidine, an organic solvent in the binder (filler)
O/R	Oxidation/reduction peak pairs in CV profiles
PAHs	Polycyclic aromatic hydrocarbons, produced from biomass pyrolysis
PC	Propylene carbonate, an organic solvent in the electrolyte
PIBs	Potassium-ion batteries
PT	Pyrolysis temperature, in °C
PVDF	Polyvinylidene fluoride, a binder (filler) material in the electrode
SAED	Selected-area electron diffraction, a characterization technique
SEI	Solid-electrolyte interphase on the anode side
SEM	Scanning electron microscopy, a characterization technique
SHE	Standard hydrogen electrode
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscope, a characterization technique
TGA	Thermo-gravimetric analysis, a characterization technique
VOCs	Volatile organic compounds produced from biomass pyrolysis
VSCV	Variable speed cyclic voltammetry, a battery test method
XPS	X-ray photoelectron spectroscopy, a characterization technique
XRD	X-ray diffraction, a characterization technique

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Dedication

This thesis is dedicated to all family, friends,

and mentors who helped me to reach this point.

I could not have done this without your support.

Chapter 1: Introduction

1.1 Potassium-ion Batteries

1.1.1 From Li ions to K ions

Due to the consumption of fossil fuels, researchers have started developing novel stable energy storage techniques to store electricity from renewable sources, such as wind and solar power, to meet the increasingly growing energy demands. Since first commercialized in 1991, lithium-ion batteries (LIBs) have become the first choice for the rechargeable battery market due to their high energy densities and long cycling lifespans ¹. Essentially, LIBs are concentration cells following the 'rocking-chair' mechanism: Li ions deintercalate from the cathode, move through the electrolyte, and insert into the anode resulting in a Li⁺-deficit cathode and a Li⁺-rich anode during the charging process, and *vice versa* during the discharging process.

However, LIBs face a host of challenges now: slow energy density improvement, insufficient cost reductions, and unsecured resource supply ². Notwithstanding the dominance of LIBs in portable devices, electric vehicles (EVs), and hybrid electric vehicles (HEVs), LIBs are costly at present for applications in large-scale energy storage systems (ESSs) such as smart grids and public transportations ³. In fact, 40% of the LIB production cost nowadays comes from electrode materials demanding largely for lithium and transition metals (such as cobalt) ⁴. Recent studies have indicated that the ever-increasing economic prosperity in LIBs marketplace comes at a cost to the environment in the form of resource depletion.^[4] Moreover, the low crust abundance and huge consumption of lithium and cobalt resources also lift the cost of LIBs, which may one day becomes an issue, especially considering that the scarcity of lithium and some of the transition metals currently used in LIBs ⁵. As a result, novel and low-cost energy storage systems are urged to be researched and developed.

Considering the large radii and high valences of Mg²⁺ and Al³⁺ creating a strong solvation effect and hindering the insertion process, Na⁺ and K⁺ with similar physicochemical properties as Li⁺ and far richer abundance have drawn more attention. Since the 2000s, researchers have studied a variety of novel alkali metal-ion batteries. Compared with sodium-ion batteries (SIBs), studies about potassium-ion batteries (PIBs) are expected to exhibit similar excellent power density and fairly high energy density but are still in the infancy of development.



1.1.2 Working principles of Potassium-ion Batteries

Figure 1 Working principles of PIBs. Reprinted with permission of 2020 Elsevier B.V.

Due to the decent energy density and high power density at a low cost, PIBs have appeared as a promising substitute for large-scale energy storage applications. **Figure 1** shows both macroscopic and microscopic processes of a PIB in the C/D process. The electricity produced from clean energy such as wind power and solar power can be stored as chemical energy in PIBs in the charging process. To be more exact, electrons move from the cathode (*ex.* K₂Mn[Fe(CN)₆]) to the anode (*ex.* HC) via an external circuit while K ions as internal charge carriers migrate to the anode through the electrolyte and separator, creating electromotive forces and a huge potential gap. In discharging process, K ions escape from the anode, diffuse through the separator and eventually land in the cathode, while the electrons flow through the external circuit and power the electrical appliances.

1.1.3 Merits of Potassium-ion Batteries

First, the cost of PIBs can be largely cut down, considering the abundant resources and cheap anodes. Potassium is the second most abundant element among alkali and alkaline earth elements in the earth's crust (Ca>Na≈K>Mg>...>Li), bringing in a cost-benefit ^{6,7}. As listed in Table 1, the crust abundance of potassium is 1.5 wt.%, close to sodium (2.3 wt.%) and 1,000 times larger than that of lithium (17 ppm); potassium carbonate costs US\$1,000 per ton versus US\$6500 of Li₂CO₃⁸; the cost of industrial-grade potassium (US\$13,000 per ton) is one order of magnitude lower than lithium. Moreover, the transitional metal compounds in cathode synthesis for PIBs (such as manganese, iron, vanadium) are cheaper than cobalt, which is generally used in commercial LIBs. Similarly, K salts in the electrolyte have a lower cost than Li-salts. For example, the cost of KPF₆ (US\$338 per kg) is only <5% of LiPF₆ (US\$7,113 per kg) ⁹. Besides, instead of overpriced copper, aluminum can be used in PIBs as the current collector because potassium metal does not form an alloy with aluminum, reducing both the cost and the weight. In a full cell, cheaper hard carbon (HC) from a facile pyrolysis method is commonly used as the anode in PIBs, while graphite synthesized with multi-steps as a commercial anode for LIBs is generally more expensive. Furthermore, in the battery industry, safety and stability are also one part of the cost-reduction strategy. Many studies have presented high reversible charging/discharging (C/D) capabilities of PIBs with at least 500 cycles before 80% of capacity retention ¹⁰⁻¹⁴.

Table 1	1 Physical a	nd chemical	properties of	of lithium,	sodium,	and potase	sium el	lements.	Reprinted
with pe	ermission o	f 2020 Elsevi	er B.V.						

Properties	Lithium	Sodium	Potassium
Atomic number	3	11	19
Atomic mass (g mol ⁻¹)	6.941	22.9898	39.0983
Density at 25 °C (g cm ⁻³)	0.534	0.97	0.89
Ionic radius (Å)	0.76	1.02	1.38
Crust abundance (wt.%)	0.0017	2.3	1.5
Crust abundance (mol.%)	0.005	2.1	0.78
Cost of carbonate (US\$ ton ⁻¹)	6,500	200	1,000
Cost of industrial grade metal (US\$ ton ⁻¹)	100,000	3,000	13,000
Cost of APF ₆ (US $\$ kg ⁻¹) ⁹	7,113	2,589	338
Cost of AClO ₄ (US\$ kg ⁻¹) ⁹	2,119	282	248
$E^{0}\left(A^{+}_{aq}/A\right)vs.$ SHE (V) 15	-3.040	-2.714	-2.936
$E^{0}\left(A^{+}_{PC}/A\right)vs.$ SHE (V) 15	-2.79	-2.56	-2.88
$E^{0}\left(A^{+}_{\text{EC/DEC}}/A\right)$ vs. $\text{Li}^{+}_{\text{EC/DEC}}/\text{Li}\left(V\right)^{16}$	0	0.3	-0.15
Strokes' radius in EC (Å) ¹⁷	1.95	2.34	2.36
Strokes' radius in PC (Å) ¹⁷	4.8	4.6	3.6
Solvation energy in EC (eV) ¹⁸	5.85	4.76	4.12
Desolvation energy in PC (eV) ¹⁹	2.24	1.65	1.24
Desolvation energy in EC (eV) ¹⁹	2.17	1.59	1.19
Desolvation energy in DEC (eV) ¹⁹	2.14	1.54	1.09
Desolvation energy in EMC (eV) ¹⁹	2.07	1.49	1.06
σ_{A}^{+} in 0.8 M APF ₆ -PC (mS cm ⁻¹) ²⁰	4.38	6.38	6.55
σ_A^+ in 1 M AFSI-EC/DEC (mS cm $^{-1}$) 16	9.3	9.7	10.7
σ_A^+ in 1 M APF ₆ -EC/DMC (mS cm ⁻¹) ²¹	9.8	10	11.5
σ_A^+ in 1 M AFSI-DME (mS cm ⁻¹)	16.9 ²²	16 ²³	13.1 ²⁴
D_{A}^{+} in graphite (×10 ⁻⁹ cm ² s ⁻¹)	9 ²⁵		0.6 26
D_{A}^{+} in HC (×10 ⁻⁹ cm ² s ⁻¹)	2.1 ²⁷	1 ²⁸	1.2 ²⁸

Second, PIBs can generate high potentials because of the relatively lower redox potential of K⁺/K. The potential of the K⁺/K redox pair (-2.936 V versus the standard hydrogen electrode [SHE]) is comparable to that of Li⁺/Li (-3.040 V), much lower than Na⁺/Na (-2.714 V). The low redox potential of K⁺/K gives high operational voltages of PIBs and ensures even high energy density. Remarkably, the standard potential of K⁺/K (-2.88 V versus SHE) is even 0.09 V lower than that of Li⁺/Li (-2.79 V) in propylene carbonate (PC) ¹⁵. Even in the mixture of ethylene carbonate (EC) with diethyl carbonate (DEC), the redox potential of K⁺/K is also 0.15 V lower than that of Li⁺/Li¹⁶. In this way, PIB systems are advantageous for higher operational voltage than LIBs, dissimilar to SIBs and Mg-ion batteries ¹⁶. Taking K₀FeSO₄F cathode reaction as an example, which was obtained via the electrochemical oxidation of KFeSO₄F by assembling a Li/KFeSO₄F cell, the potential of K⁺ intercalation/deintercalation was 4.0 V versus K⁺/K, higher than 3.7 V of K₀FeSO₄F (versus Li⁺/Li) and 3.4 V of K₀FeSO₄F (versus Na⁺/Na) ²⁹. We recently discovered that fluorinated carbons (CF0.88) as cathodes have an even higher energy density of 805 Wh kg-1 at 2C in K cells than in Li cells (776 Wh kg⁻¹) ³⁰. It is worth noting that the lower standard reduction potential of K⁺/K (-2.88 V) than -2.56 V for Na⁺/Na in carbonate solvents allows for forming a stage-I intercalation compound (KC₈) at an average operational potential of ca. 0.3 V versus K⁺/K, realizing a specific capacity of 250 mAh g⁻¹ at a fully discharged state; however, Na-ion storage in graphite is difficult to achieve ^{15, 16}. A breakthrough was made by Ji and coworkers, who reported a reversible K-ion intercalation/deintercalation behavior in graphite, presenting the feasibility of transferring the well-developed LIBs to the low-cost PIBs ³¹. As a result, despite the limited capacity of PIB cathodes, higher energy densities of PIBs can be compensated by their higher operational potentials.

Third, fast ionic kinetics of K ions in the electrolytes ensures high rate performances of the C/D process at high current densities, and thus high power densities can be realized. Studies indicate that although K⁺ has the largest ionic radius (1.38 Å) compared with Li⁺ (0.76 Å) and Na⁺ (1.02

Å), K⁺ has the smallest Stokes' radius (3.6 Å) compared with Li⁺ (4.8 Å) and Na⁺ (4.6 Å) in PC solvents ¹⁷. As a result, K⁺ has the highest ion mobility and ionic conductivity (Table 1). The mechanism has been studied in detail: due to the lower charge density, larger-sized K ions have less Lewis acidity than Li-ions and Na ions, leading to smaller solvated-K ions with limited Stokes' radius in liquid electrolytes, which renders the higher ionic mobility, more significant transference number and lower desolvation energy. Hence, K⁺ exhibits faster ionic diffusion kinetics than Li⁺ and Na⁺. This can be further proved by the higher ionic conductivity of K⁺ in both aqueous and non-aqueous electrolytes ³²⁻³⁴. Based on the above advantages, replacing Li⁺ with K⁺ will enable batteries to achieve improved rate performance and higher loading without sacrificing specific capacity. Moreover, K ions have the lowest desolvation energy compared with Li-ions and Na ions in many liquid electrolytes (*e.g.*, PC, EC, DEC, DMC in **Table 1**), leading to good ionic kinetics and thereby promising rate capability ³⁵.

1.2 Hard Carbon Anode

To date, various categories of anode materials have been studied and exhibited stable K-ion storage capacity, including soft carbon ³⁶, HC (*e.g.*, pyrolysis carbon, acetylene black) ^{37, 38}, metal and metallic oxides (*e.g.*, alloy) ^{39, 40}. HC with hybrid structures of both layered graphite-like units and sufficient deficiencies can generate a high and reversible specific capacity, owing to the dual K-ion storage mechanisms of bulk insertion and surface adsorption ^{41, 42}. Bulk insertion is a typical Li-ion storage mechanism of graphite in LIBs, while surface absorption is a diffusion-controlled process generally utilized in supercapacitors. Fine control of HC structure is a key to achieving bulk insertion and surface adsorption simultaneously to realize optimal ion storage performance. Biomass is an abundant and low-cost source for HC fabrication and is mainly composed of cellulose, semi-cellulose, and lignin. In the paper industry, tons of lignin are disposed of as waste (black liquor) or burned as a low-grade fuel. Some studies suggested the excellent ion storage capacity of lignin-derived hard carbon (LHC) in LIBs, SIBs, and PIBs ^{43, 44}.

Moreover, several studies have successfully derived HC for PIBs directly from other biomass, such as soybeans ⁴⁵, loofah ⁴⁶, maple leaves ⁴⁷. In detail, loofah-derived HC has exhibited a stable specific capacity of 200 and 100 mAh g⁻¹ at 100 mA g⁻¹ in LIBs and PIBs, respectively ⁴⁶. However, the K-ion storage performance of LHC varies significantly in different works ⁴⁸, probably due to various pyrolysis conditions and lignin precursors used.

It is well known that the electrochemical performance of LHC is highly dependent on its microscopic structure. Previous studies have focused on investigating the effect of pyrolysis conditions, especially pyrolysis temperatures, on the structure and electrochemical performance of HCs, which, however, exhibited distinct ionic storage properties. Since lignin itself has different degrees of polymerization from its three monomers ⁴⁹, we speculate that the electrochemical performance of LHCs may rely on the pyrolysis conditions and depend on the lignin precursor used. Nevertheless, lignin precursors' influence on the derived LHCs, their electrochemical performance, and ion storage mechanism has been seldom studied. We believe that the interplay among lignin structure (molecular weight), pyrolysis condition, and LHC structure is essential for achieving excellent K-ion storage performance but remains unveiled, to the best of our knowledge. Therefore, herein, we adopted three types of technical-grade lignin with molecular weights of 2233 (low MW), 9660 (medium MW), and 14300 g mol⁻¹ (high MW) as a model system to systemically investigate and clarify the role of lignin structure and pyrolysis condition in determining hard carbon structure, K-ion storage performance, and K-ion storage mechanism in PIBs. It is found that the structure of LHC is determined by both lignin's MW and PTs. These different structures significantly impact their K-ion storage performance, especially on the two Kion storage behaviors (bulk insertion and surface adsorption). Among all LHCs, the one derived from medium-MW lignin at 700 °C, noted as M700, exhibited the best overall performance. It achieved a high reversible specific capacity of ~300 mAh g⁻¹ and ~170 mAh g⁻¹ at 50 and 200 mA g⁻¹, and high capacity retention of 80% after 100 cycles, which meets the technical requirements

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of the anode materials in PIBs. Considering the cost-effectiveness, LHC shows promising prospects in practical battery applications.

1.3 Electrolyte Chemistry

The 'solvation effect' in electrolytes enables K ions to diffuse smoothly at high current rates ¹⁸. Although K ions have larger ionic radii (1.38 Å) than Li ions (0.76 Å) and Na ions (1.02 Å), K ions have the smallest Stokes' radii (3.6 Å) compared with Li ions (4.8 Å) and Na ions (4.6 Å) in PC as a non-aqueous solvent ¹⁷. Therefore, K ions diffuse with less kinetic resistance than Li ions and exhibit relatively low standard potentials in popular organic solvents – the redox potential of K⁺/K is 0.15 V lower than that of Li⁺/Li in the mixture of EC/DEC – which promise potential high power density of PIBs ¹⁶.

As the most popular carbonaceous anode in PIBs, HC can realize high specific capacity at a low cost. Depending on the facile fabrication process, the structure of HC is adjustable to maximize the storage of different charge carriers. The surface-adsorption and bulk-insertion contributions can also be tailored for battery and supercapacitor applications. However, due to K⁺-solvent chelation co-intercalation, HC anodes without surface modification often suffer from severe structural damage and capacity fading during cycling, which is the main obstacle towards commercialization. Electrolytes contribute to solid-electrolyte interphase (SEI) formation and Kion diffusion by decomposition and solvation effect. A reliable and elastic SEI can effectively suppress the capacity degradation and prevent irreversible side reactions ²⁶. PIB electrolytes often contain K salts and organic solvents (with additives). Popular K salts are KPF₆, KClO₄, KBF₄, $KN(SO_2F)_2$ (potassium bis(fluorosulfonyl)imide, KFSI), and KN(SO₂CF₃)₂ (potassium bis(trifluoromethanesulfonyl)imide, KTFSI). Carbonate ester and ether solvents, such as EC, DEC, and dimethoxyethane (DME), are often divided into chains and rings from the carbon arrangement. In this thesis, we report the macroscopic electrochemical effect of electrolytes on HC anodes and investigate the microscopic degradation mechanisms of HC in different electrolytes, especially the synergic contribution of inorganic anions (*e.g.*, FSI⁻) and organic solvents (*e.g.*, EC and DEC) in SEI formation and K-ion solvation/desolvation *via* electrochemical tests and characterization techniques.

1.4 Research Gaps and Novelty

PIBs have been studied as a novel beyond-Li battery system since 2004. HC is known as one of the most promising anode materials for PIBs. Many studies reported biomass-derived HC anodes with excellent electrochemical performance in PIBs. However, few discussed the correlation between biomass MW, pyrolysis conditions, and the storage mechanism at a structural level. Therefore, we used lignin as a showcase and showed that lignin MW indeed impacts the HC structure via multiple characterizations. According to the electrochemical tests and kinetics analysis result, I quantified the K-ion storage contribution of bulk insertion and surface adsorption for each LHC. The mechanism was summarized to provide our perspectives for future biomass-derived HC research.

Additionally, previous studies on PIB electrolytes have not explained the electrolyte effects on HC anodes at a very detailed level. However, it is essential to understand the capacity degradation mechanisms of HC anode in each electrolyte so that we can predictably magnify PIB's potentials by rational electrolyte design and optimization. This is the first study that systematically compares electrochemical differences contributed by common electrolytes and clarified the roles of electrolytes in PIBs at such a detailed level. From the viewpoints of solvation effect and ionic diffusion, solid-electrolyte interphase (SEI) formation, co-intercalation, and charge transfer kinetics. The main finding was that KFSI in EC/DEC electrolyte enabled maximal capacity and cycling stability of hard carbon due to elastic inorganic-rich SEI and excellent charge transfer kinetics from FSI- decomposition and complete K⁺(EC)₂ solvation. This study is significant for the field of PIBs because it not only tackled the HC-electrolyte compatibility problem, an urgent

scientific issue in PIBs but also provided guidance on the deep understanding of electrolyte functionality and design of new electrolyte systems for PIBs.

1.5 Research Objectives

The goal is to convert lignin into HC anode in PIB applications and investigate: 1) the molecular weight effect of lignin in determining LHC electrochemical performance, 2) the kinetics behaviors of K-ion storage in LHC anodes with different structure, and 3) the electrolyte functions in improving the cycling stability of PIBs.

1.6 Summary

In this thesis, chapters 1 and 2 are the introduction and methodology (the experimental part). Chapters 3 and 4 are the results and discussion about two research projects: LHC anodes in PIBs and the electrolyte chemistry effect, respectively. In the end, conclusions and perspectives, including limitations of this work, contributions of this work, and recommendations for future work, are given out.

Chapter 2: Methodology

2.1 Materials and Sample Preparation

Technical-grade lignin with different degrees of polymerization (low MW = 2233 g mol⁻¹, medium MW = 9660 g mol⁻¹, high MW = 14300 g mol⁻¹) were provided by Advanced BioCarbon 3D Ltd (BC, Canada) and were used as the carbon precursors as received. As shown in **Figure 2**a, lignin is composed of three interconnected monomers: sinapyl alcohol (denoted as S in Figure 2b), coniferyl alcohol (G), and minor p-coumaryl alcohol (H). They have similar molecular structures while S-monomer has two -OCO₃ functional groups, G-monomer has one, and H-monomer has none [25]. Pyrolysis, a facile carbon fabrication method, was applied to convert lignin into hard carbon in Figure 2c. In a tubular furnace, lignin with low, medium, and high MWs was pyrolyzed at 500, 600, 700, 800, 900, and 1000 °C for 2 hours with a heating rate of 5 °C min⁻¹ under a nitrogen atmosphere. Without rinsing and further activation, LHC products, labeling as a letter (for lignin's MW) plus a number (pyrolysis temperature), were directly ground into a powder and used as active anode materials in half K//LHC cells (CR2032).



Figure 2 Three monomers (a) interconnect and co-build lignin (b) with different degrees of polymerization (low, medium, and high MW). Six pyrolysis temperatures from 500 °C to 1000 °C were applied to produce lignin-derived hard carbon (HC) (c).

2.2 Material Characterizations

Multiple characterization techniques were used in this thesis, such as scanning electron microscopy (SEM), high-resolution transmission electron microscope (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), selected-area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectrometer, thermo-gravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) method. Tescan Mira 3 XMU tested SEM; Cameca SXFive Field Emission EPMA was employed for the X-ray mapping. FEI F30 recorded the HRTEM with HAADF-STEM, SAED, and EDS. XRD spectrum was measured by Bruker D8-Advance X-ray diffractometer using Cu K α radiation (λ = 1.5418 Å) with a scan step of 0.02° in the 2 θ range of 10–90°. XPS was recorded by Axis Ultra DLD from Kratos Analytical. Raman spectra were recorded by HORIBA Scientific LabRAM Raman spectrometer equipped with a 532.03 nm laser source. TGA was measured under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹ from room temperature (~20 °C) to 700 °C. Nitrogen absorption and desorption isotherms data were collected using TriStar II 3020 and analyzed using the BET method to calculate the surface parameters, e.g., the mean pore diameter and specific surface area.

2.3 Battery Assembly

In preparation of the electrode slurries, 80 wt.% of LHC as the active material and 10 wt.% of Super P as a conductive additive were mixed by grinding for 30 minutes. 10 wt.% of PVDF dissolved in N-methyl-2-pyrrolidine (NMP) was then added as a binder (filler). After grinding for three more minutes, the slurries were coated onto aluminum foils and dried in a vacuum drying oven at 60 °C for 12 hours. Coated Al foils were punched into round electrodes with a diameter of 12 mm and an average loading of 1.0–2.0 mg cm⁻² of the active materials. Before putting the electrodes into glove boxes, these electrodes were further dried at 110 °C for 12 hours. In a K//HC half-cell, LHC anodes were the working electrodes; K metal (cell-level purity) was the counter

electrode, and 0.8 м KFP₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol.) was used as the electrolyte. Later, four electrolytes including 0.8 м KFP₆ in EC/DEC (1:1 vol.), 1.0 м KFSI in EC/DEC (1:1 vol.), 1.0 м KFP₆ in DME, and 1.0 м KFSI in DME was used for K//M700 half cells. A glass microfiber filter (Whatman, Grade GF/D) was used as the separator. All assembly process was carried out within the glove box at 99.99% Argon gas atmosphere.

2.4 Electrochemical Tests

In order to test the electrochemical performance of LHC anodes, multiple techniques were employed. Galvanostatic charge/discharge (C/D) measurements were tested at a voltage window of 0.01–3 V at a current density of 50 mA g⁻¹ using a Neware battery testing system (BTS 4000). Rate performance was tested at current densities of 20, 50, 100, 200, and 20 mA g⁻¹. Electrochemical impedance spectroscopy (EIS) was tested in a frequency range of 10 mHz ~ 0.1 MHz with an amplitude of 10 mV. Galvanostatic intermittent titration technique (GITT) was performed with 5 min of charging/discharging and 50 min of resting at 100 mA g⁻¹. Variable speed cyclic voltammetry (VSCV) was measured by Biological SP-150 Potentiostat EIS station between 0.01–3 V at scanning rates of 0.1–50 mV s⁻¹.

Chapter 3: Lignin-derived Hard Carbon Anodes in Potassium-ion Batteries

PIBs have drawn much attention as an energy storage system for large-scale grid applications due to their high energy density and low cost. As the most promising anode material for PIBs, HC has been prepared from various sources but exhibited varying electrochemical performance, probably due to a limited understanding of materials structure and K-ion storage mechanisms. Biomass (such as lignin) represents an abundant source for synthesizing HC; however, few studies have investigated the role of lignin molecular weight (MW) in determining HC's structure and K-ion storage mechanism. Herein, we developed a series of LHCs from lignin with different MWs at serial PTs and correlated the lignin MWs and PTs with LHC structure, electrochemical performance, and K-ion storage mechanisms. The best-performed LHC delivered a high reversible specific capacity of ~300 mAh g⁻¹ at 50 mA g⁻¹ and was denoted as M700 since it was derived from medium-MW lignin (9660 g mol⁻¹) at 700 °C. M700 exhibited a mixture structure of graphite-like nanocrystals with the largest interlayer distance and amorphous area, which maximized the K-ion storage capacity from both bulk-insertion and surface-adsorption mechanisms.

3.1 Correlation among Lignin Molecular Weights, Pyrolysis Temperatures, and Hard Carbon structures

Previous studies have shown that pyrolysis temperature plays a critical role in determining the eventual structures of LHCs and HCs derived from other biomass precursors ⁵⁰. However, the effect of lignin precursors and molecular weight on the LHCs was rarely discussed. Therefore, the first experimental part of this thesis is to clarify the influence of both pyrolysis temperature and molecular weight on the morphology and structure of LHCs.



Figure 3 SEM images of raw lignin with (a) low MW, (e) medium MW, (i) high MW, and HCs derived from the lignin by pyrolysis at 500 °C (b, f, j), 700 °C (c, g, k), and 1000 °C (d, h, i).

Figure 3 displays the typical SEM morphologies of pristine lignin and LHCs derived at 500, 700, and 1000 °C. All three pristine lignin show a similar compact structure (Figure 3a, 3e, 3i). However, the LHCs show distinct morphologies, exhibiting a strong dependence on both lignin molecular weight and pyrolysis temperature. All the LHC particles derived from low-MW lignin (L500, L700, and L1000) possess irregular shapes with a mirror-like smooth surface (Figure 3b, 3c, 3d), indicating their high density and low porosity. For the medium-MW lignin, M500 and M700 pyrolyzed in the medium temperature range (500–700 °C) possess a hierarchical porous structure and have numerous pores in the structure (Figure 3f, 3g). However, a higher pyrolysis temperature (1000 °C) results in a denser structure with less visible pores in M1000 (Figure 3h).

For the high-MW lignin, the LHCs (H500, H700, and H1000) exhibit no apparent difference in the morphology and have some visible pores on the surface. From Figure 3, it can also be found that at medium pyrolysis temperatures (500–700 °C), HCs derived from the medium-MW lignin display the most porous structure among all the samples, as also shown in the lower magnification in Figure 4. BET analysis discloses the specific capacity area of L700, M700, and H700 is 6.1, 12.3, and 0.71 m² g⁻¹, respectively, suggesting the relatively low surface area of all three samples.



Figure 4 Scanning electron microscope (SEM) images (a–c) and EDX elemental mapping (d) of M700.

The structures of LHCs derived from the three lignin precursors are characterized by X-ray diffraction (XRD) and Raman spectroscopy, as presented in **Figure 5**. Figure 5a shows the XRD patterns of the LHCs from low, medium, and high-MW lignin pyrolyzed at 500, 700, and 1000 °C.

All the XRD patterns display two broad peaks centered at about 25° and 43°, which are assigned to the (002) and (010) planes of graphite (JCPDS PDF No. 08–0415), respectively. In Figure 5a, it can be found that the peak position of the (002) plane of LHCs varies with pyrolysis temperature. For each group of LHCs, the (002) peak experience a left shift to lower 20 degrees with pyrolysis temperature in the order of 500, 1000, and 700 °C. This change suggests that the interlayer distance of carbon layers in HCs first increases with pyrolysis temperature from 500–700 °C, and decreases with the temperature further elevated to 1000 °C. The broad XRD peaks suggested the slightly varied interplanar distance among graphitic nanocrystals with highly defective layers. Averagely, according to Bragg's law ⁵¹, d₍₀₀₂₎ interlayer distance is calculated and plotted in Figure 5c. Among all the samples, M700 exhibits the highest interlayer distance of 4.04 Å, which is much greater than that of graphite (3.35 Å). The considerable interlayer distance provides adequate space for both K-ion insertion and diffusion during the potassiation process. Furthermore, it is found that LHCs derived from high-MW lignin undergo a more subtle change in the interlayer distance than the other two LHCs as the pyrolysis temperature changes, suggesting the slowest growth of graphite nanocrystals in high-MW LHCs.

Raman spectroscopy is further used to extract information on the distribution of first-order Raman bands and carbon structure of lignin-derived HCs. Figure 5b presents the normalized Raman spectra of LHCs from low, medium, and high-MW lignin at 500–1000 °C. As seen, the Raman spectra for all samples consist of one D band at 1350 cm⁻¹ corresponding to the breathing model of *sp*², and one ordered G peak at 1580 cm⁻¹ assigning to the vibration mode of both rings and chains ⁴³. It can be found that the intensity of the D band, relative to the G band, increases with the pyrolysis temperature, indicating the rise of defects and disordered carbon in LHCs. For hard carbon materials, it has been reported that the D and G Raman peaks are the superposition of four sub-bands ^{52, 53}, *i.e.*, D, D1, D2, and G (Figure 2e), originating from the in-plane disorder (A_{1g} symmetry), in-plane disordered/impurities (A_{1g} symmetry), diamond-like carbon (sp³- hybridized carbon), and in-plane C-C stretch (E_{2g} symmetry), respectively. The normalized area of each band is displayed in Figure 5f. It can be found that in each group of HCs, the portion corresponding to D and D1 peaks (disordered carbon and impurities) increases as the pyrolysis temperature grows from 500–800 °C (stage I), and then decreases when the pyrolysis temperatures are higher than 800 °C (stage II). However, the G peak exhibits a reversed tendency as the pyrolysis temperature increases. The quantitative Raman analysis (Figure 5f) reveals that at pyrolysis temperatures of 800–900 °C, the in-plane disorder carbon and impurities reach maximum in lignin-derived HCs, while in-plane plane carbon (or graphite-like nanocrystals) arrives minimum for all LHCs derived from different lignin.

The cluster size of graphite-like nanocrystals in LHCs can be estimated by using the Ferrari-Robertson method for amorphous carbonaceous carbon ⁵⁴:

$$\frac{I(D)}{I(G)} = C'(\lambda) \times L_a^2 \tag{1}$$

Where C' (514 nm) corresponds to 0.0055 Å⁻¹, I(D) and I(G) refer to the intensity ratio of D and G peaks, and L_a represents the cluster size of the nanocrystals. As shown in Figure 5d, the values of L_a for LHCs increase from ~1.1 nm at 500 °C to 1.4 nm at 1000 °C but stay in the same nanometer range. Moreover, the values and trend of L_a have little independence on the lignin molecular weight; they are mainly affected by the pyrolysis temperature. The Raman analysis suggests that the number of graphite-like nanocrystals, rather than the size, varies with pyrolysis temperature elevation. As revealed in Figure 5f, the relative ratio of graphite-like nanocrystals to other types of carbon decreases from 500–800 °C (stage I) and then increases above 800 °C (stage II).


Figure 5 X-ray diffraction (XRD) patterns (a), Raman spectra (b), calculated interlayer distance (c), and nanocrystal size (d) of the HCs derived from low-, medium-, and high-MW lignin. Exemplary peak fitting of the Raman spectrum of HC-700s (e); normalized area of each peak (D, D1, D2, and G in e) for HC-700s (f).

Based on the above results, the influence of pyrolysis temperature and lignin molecular weight on the HC structure can be explained as follows.

3.1.1 Pyrolysis Temperature

As the pyrolysis temperature increases from 500 °C to 700–800 °C, disordered carbon structure (in-plane disorder and impurities, D and D1) significantly increases in all LHCs, due to the promoted pyrolysis of lignin precursors into carbon structure at elevated temperatures. The increasing formation of disordered carbon is believed to be responsible for the enlarged interplanar distance of carbon layers, as observed in the XRD (Figure 2a and 2c). As the pyrolysis temperature further increases beyond 800–900 °C, the disordered carbon atoms will be rearranged into graphite-like nanocrystals, leading to reduced interlayer distance (Figure 2c). As the temperature reaches 1000 °C, the disordered carbon structure experiences a pronounced drop in all LHCs, suggesting graphitization taking dominance at high temperatures.

According to previous studies, biomass materials undergo three-stage structural changes, *i.e.*, depolymerization, fragmentation, and amortization, during the pyrolysis process ⁵⁵. In detail, depolymerization is the break of the bonds between monomer units in lignin. This process mainly occurs at 300–500 °C and produces guaiacols (form G-lignin) and syringol (from S-lignin) ⁵⁶. Fragmentation proceeds at 400–450 °C, where the reactions of functional groups and covalent bonds start emitting volatile organic compounds (VOCs), which increases the carbon percentage (Table 2) and creates nanopores and micropores later. At >700 °C, high temperatures break the strong C-C side bonds with the production of aromatic compounds, such as benzene, phenol, and polycyclic aromatic hydrocarbons (PAHs), resulting in the rearrangement of carbon atoms into graphite-like nanocrystals ⁵⁷.

Sample ID	MW (g/mol)	Temps (°C)	C (wt.%)	O (wt.%)	S (wt.%)	Other elements (wt.%)
LO	2233	NA	80.7	19	0.3	/
L500	2233	500	93.1	6.7	0.2	/
L700	2233	700	99.5	/	0.5	/
L1000	2233	1000	99.8	/	0.2	/
MO	9660	NA	79.5	20.3	0.2	/
M500	9660	500	99.8	/	0.2	/
M700	9660	700	92.6	7	0.4	/
M1000	9660	1000	92.5	6.6	0.1	0.6 K
H0	14300	NA	74.9	24.8	0.2	/
H500	14300	500	92.7	6.4	/	0.7 K, 0.2 Mg
H700	14300	700	94.4	3.6	0.4	1.6 K
H1000	14300	1000	94.6	4.4	/	1.1 K

Table 2 Element proportions in LHCs.

Therefore, two main competing processes exist for carbon structure formation in the ligninderived HC during the pyrolysis process. First, depolymerization, fragmentation, and amortization of lignin occur at low and medium temperatures (500-800 °C), which causes the formation of a disordered carbon structure. Secondly, the elevated temperature leads to the graphitization of disordered carbon and the formation of graphite-like nanocrystals, as revealed by the growth of L_a (Figure 5d). At low and medium temperatures (500–800 °C), the formation of disordered carbon structure outperforms the formation of graphite-like nanocrystals, leading to increased interlayer distance (Figure 5c) and normalized area of D/D1 peaks (Figure 2f). At temperatures above 800 °C, the majority of lignin precursors have been turned into carbon materials, and thus the formation of graphite-like nanocrystals take dominance, resulting in the decreased interlayer distance (Figure 5c) and reduced D and D1 normalized area (Figure 2f). It is noteworthy that the trend of I_D/I_G ratio as a function of temperatures for lignin is opposite to that of graphitized carbon, such as carbon nanotubes and graphene ⁵⁸⁻⁶⁰. As reported previously, I_D/I_G ratios of carbon nanotubes and graphene decreases as the treatment temperature increases because of the elevated graphitization degree of carbon structure at high temperatures. In contrast, lignin first transforms disordered carbon via depolymerization, fragmentation, and amortization. As a result, the I_D/I_G ratio of LHCs experiences an increase with pyrolysis temperature.

3.1.2 Lignin's Molecular Weight

Lignin precursors' molecular weight significantly impacts the disordered degree of LHCs under the same pyrolysis condition. At low pyrolysis temperatures, the normalized area of D and D1 peaks (in-plane disordered carbon and impurities) is similar for LHCs from high-MW lignin as those from low- and high-MW lignin. At high pyrolysis temperatures (1000 °C), the D and D1 peak area difference becomes much more significant for these three lignin-derived HCs. The different capabilities of lignin precursors might explain this in depolymerization and fragmentation, which are the starting point of the formation of disordered carbon. In general, low-MW lignin is relatively

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easier to get fully depolymerized and fragmented than for high-MW lignin under the same pyrolysis condition. This is verified by TGA analysis in Figure 6. Compared to medium- and high-MW lignin, low-MW lignin exhibits dramatic weight loss at low temperatures, indicating small clusters of lignin are more comfortable to be depolymerized and fragmented ⁶¹. In other words, low-MW lignin-derived HCs would experience more rapid transformation from disordered carbon to graphite-like nanocrystals at low temperatures than high-MW lignin-derived HCs. The higher the molecular weight of lignin, the slower transformation from lignin to disordered carbon.



Figure 6 TGA curves of three raw lignin samples.

HRTEM characterization on L700, M700, and H700 was performed to verify the influence of lignin molecular weight on the carbon structure. **Figure 3** presents the TEM, HRTEM, SAED patterns, and EDX elemental mapping images of the three samples. As shown in Figure 7a-c, L700, M700, and H-700 particles consist of many primary particles with diameters of 10-20 nm. In particular, M700 particles contain many nanopores due to their relatively high surface area (12.3 m² g⁻¹), which could provide diffusion channels for the electrolyte and accommodate more K ions during the potassiation process. HRTEM images in Figure 7d-f disclose that graphite-like nanocrystals area decreases as the molecular weight of lignin increases. L700 possesses many

graphite-like, multilayered carbon spheres with an interlayer distance of ~3.28 Å. M700 shows fewer graphite-like nanocrystals with an enlarged interlayer distance of ~3.45 Å and many disordered regions. In contrast, H700 consists of a mainly amorphous-dominated structure, as shown in Figure 8.



Figure 7 Transmission electron microscopy (SEM) images (a-c), high-resolution TEM (HRTEM) images (d-f), and EDX elemental mapping (g, h, i) of L799, M700, and H700.

Therefore, the HRTEM analysis confirms that low-MW lignin tends to develop graphite-like nanocrystal structures than high-MW ones. Under the same pyrolysis condition, lignin with a higher MW would yield HCs with a more disordered carbon structure and more considerable carbon interlayer distance, consistent with the Raman analysis. According to the element mapping in Figure 7g-i, the main elements in L700, M700, and H700 are all C, N, and O, which is reasonable considering lignin as a biomass carbon precursor.



Figure 8 High-resolution transmission electron microscope (HRTEM) images of HC-700s.

3.2 K-ion Storage Performance of Lignin-derived Hard Carbons

The electrochemical performance of LHCs was evaluated as the anode for PIBs in a half-cell configuration with K metal as the counter electrode. The influence of both pyrolysis temperature and lignin molecular weight on the cycling performance of LHCs was systemically studied, and the results are compared in **Figure 9**. Overall, all LHCs show reversible K-ion storage properties during the potassiation and de-potassiation process and undergo capacity degradation to different

extents. Moreover, the K-ion storage performance of HCs exhibits evident dependence on the pyrolysis temperature and lignin molecular weight. HCs derived from low-MW lignin exhibit initial capacities of around 350–480 mAh g⁻¹ but experienced rapid capacity decay in the following cycles. The specific capacity remains below 50 mAh g⁻¹ after 100 cycles, indicating the low K-ion storage capacity and cycling performance of low-MW LHCs.



Figure 9 Cycling performance of L-HCs (a), M-HCs (b), and H-HCs (c) derived at pyrolysis temperatures from 500 °C to 1000 °C, cycling performance comparison of L700, M700, and H700 (d). All samples are measured at a current density of 50 mA g⁻¹.

Overall, L700 and L1000 show similar cycling stability and specific capacity (Figure 9a). LHCs derived from medium-MW lignin demonstrate the best electrochemical performance towards K-ion storage among all the samples synthesized from the three types of lignin. The reversible capacity of LHCs gradually increases from 100 mAh g⁻¹ for M500 to ~300 mAh g⁻¹ for M700. A further rise in the pyrolysis temperatures leads to lower specific capacities (M800 and M900). Compared to L700, M700 shows much-improved cycling stability over 100 cycles and can maintain a specific capacity of 200 mAh g⁻¹ after 100 cycles (Figure 9b). The electrochemical performance of LHCs derived from high-MW lignin fall between those from low-MW and medium-MW lignin. The best performing HCs are H700 and H900 (Figure 9c). Although H700 exhibits high initial capacities, it can only deliver a reversible capacity of 92 mAh g⁻¹ after 100 cycles.



Figure 10 Coulombic efficiency (CE) L-HCs (a), M-HCs (b), H-HCs (c), and HC-700s (d).

It should be noted that all the samples have significant capacity drop and low Coulombic efficiency (CE) in the first few cycles (**Figure 10**), probably due to the decomposition of electrolytes and the formation of solid-electrolyte interphase (SEI) ^{62, 63}. In Figures 9a-c, it can be found that pyrolysis of all three lignin at 700 °C yields the best K-ion storage performance in terms of reversible capacity, cycling stability, and CE. Low pyrolysis temperature results in low K-ion storage capacities, most likely due to the incomplete decomposition of polymer precursors. High pyrolysis temperature leads to the worse electrochemical performance of HCs derived from medium one. Figure 9d compared the cycling performance of L700, M700, and H700. It is evident that M700 outperforms L700 and H700 in specific capacity and cycling stability. Therefore, lignin with medium MW is the favorable precursor for fabricating HCs for potassium-ion storage.

Since M700 exhibits the highest reversible capacity of 300 mAh g⁻¹ and capacity retention of 79% after 100 cycles, more detailed electrochemical characterizations are performed on M700 to understand its K-ion storage behavior. **Figure 11**a-b shows that M700 realizes a high initial CE of 52% and maintains a high specific capacity of ~200 mAh g⁻¹ even after 100 cycles. Moreover, the charge profiles of M700 consist of two sloped plateaus around 1.2–0.4 V and 0.4–0.1 V (Figure 11b), which correspond to the insertion of K-ion into carbon layers and the adsorption of K ions on the surface ⁶⁴. The K-ion storage mechanism is investigated in detail later. Also, M700 exhibits excellent rate performance (Figure 11c) and could deliver a specific capacity of ~304, 234, 204, and 171 mAh g⁻¹, at a current density of 20, 50, 100, and 200 mA g⁻¹, respectively. Moreover, the specific capacity can be recovered to 254 mAh g⁻¹ when the current is reversed back to 20 mA g⁻¹. With the increase of current density, M700 shows increased polarization in the charge and discharge curves. Still, it maintains the two sloped plateaus, which could be assigned to K-ion insertion and adsorption ⁵⁰. CV measurement was further performed to investigate the electrochemical process of K-ion storage in M700.



Figure 11 Cycling performance (a), charge/discharge profiles (b), rate capability (c,d), CV curves (e), and Nyquist-plots of (f) of M700 with the equivalent circuit.1

As shown in Figure 11e, the CV curves of M700 are composed of two pairs of redox peaks, *i.e.*, R1/O1 at ~0.9 V and R2/O2 at ~0.5 V, indicating the two-step K-ion storage mechanism. Compared to Li ions, it is challenging for K ions with larger ionic radii to insert into layered carbon at lower potentials ⁴⁶. K-ion adsorption behavior at the near-surface area of LHCs compensated the capacity loss at higher potentials. EIS was tested at the fully charged state of HC anodes, and the results are shown in Figure 11f. As seen, all the Nyquist plots of M700 consist of one semicircle in the medium frequency region, corresponding to the SEI resistance (R_f) and charge transfer resistance (R_{ct}), and one inclined line in the low-frequency region. The intercept of the Nyquist plots with the x-axis represents Ohm resistance (Rs). Rf, Rct, and Rs values are extracted by fitting the Nyquist plots with the equivalent circuit (inset in Figure 5f) and listed in Figure 12. During the cycling process, the Ohm resistance of K//M700 half cell remains below 10 Ω cm⁻². However, R_f (~900 Ω cm⁻²) and R_{ct} (~2500 Ω cm⁻²) are much larger than R_s and are generally increasing as the cycling number grows. More importantly, the number of R_f before cycling is nearly zero, after which the value soars into ~900 Ω cm⁻², indicating the formation of SEI layer during the 1st discharging process. Notably, two irreversible reduction peaks at 0.63 V and 0.96 V are observed in the M700 CV profile, corresponding to SEI formation in the 1st cycle.



Figure 12 Ohm resistance (Rs), SEI resistance (Rf), and charge transfer resistance (Rct) of M700.



3.3 Correlation of K-ion Storage Mechanisms with Hard Carbon Structure

Figure 13 The overall capacity of (a) L700, M700, and H700 and (b) M500, M700, and M1000 at varying scanning rates from xxx to xxx; (b); bulk-insertion (Qb) and surface-adsorption (Qs) contributions to the capacity of HC700s (c) and M-HCs (d); an example of M700 electric charge change during C/D at different scanning rates (e).

Studies indicated that HC provides reversible K-ion storage capacity (Q) in two mechanisms, *i.e.*, bulk-insertion (Q_b) and surface-adsorption (Q_s), which correspond to the insertion of K ions into carbon layers of graphite-like nanocrystals and the adsorption of K ions in the near-surface amorphous deficiencies, respectively [41]. The contributions of Q_b and Q_s are quantified by using Trasatti's method [41]:

$$Q(v) = Q_s + Q_b = Q_s + kv^{-\frac{1}{2}}$$
(2)

Where *v* is scan rate, *k* is adjustable constants. After plotting Q and $v^{-1/2}$, as shown in Figure 6a-b, the slope is the *k*, and the interception is the Q_s . By determining *k* and Q_s , I calculated the ratio of the two K-ion storage behaviors, as shown in Figure 6c-d. Figure 6e shows one example of extracting the data from M700. As the scanning rate increases from 0.1–2.0 mV s⁻¹, the bulk-insertion ratio continuously decreases from 45–73% to 0% for all the samples investigated. This trend suggests that the surface adsorption mechanism dominates K-ion storage at high current densities, while bulk-insertion and surface-adsorption mechanisms co-exist at low current densities.

The influence of lignin molecular weight on the K-ion storage mechanism is displayed in **Figure 13**a, 13c. It can be found that, at the same scanning rate, the surface-adsorption to bulk-insertion ratio is higher in LHCs derived from high-MW lignin than those from medium- and low-MW lignin. For example, at 0.3 mV s⁻¹, the bulk-insertion contribution is only 34% for H700, in contrast to 42% and 46% for M700 and L700, respectively. Regardless of scanning rates, surface-adsorption contribution is proportional to the lignin molecular weight, which, in turn, determines the carbon structure (Figure 7). Among all the three samples, H700 exhibits the highest degree of disordered carbon, which is believed to be mainly responsible for the surface adsorption of K ions. More specifically, the adsorption behavior at the near-surface defective area (*e.g.*, the active heteroatom units) should be categorized as chemical adsorption due to the existence of chemical bond formation and electron transferring; as for the pore-filling process, it is more considered

physical adsorption at nanoporous structures with the Van der Waals force. In contrast, L700 possesses the highest degree of graphite-like nanocrystals with the largest interlayer distance, contributing to the insertion of K ions into the carbon layer. As a result, L700 shows the most bulk-insertion contribution in all three samples under all scanning rates.

The effect of pyrolysis temperature on the K-ion storage mechanism is shown in Figure 13b and 13d using medium-MW LHCs as examples. At low pyrolysis temperatures, the LHCs exhibited dominating bulk-insertion mechanism for K-ion storage, probably due to the incomplete transformation of lignin precursors to carbon structure. As the pyrolysis temperature increased from 500–700 °C, the surface-adsorption contribution increased dramatically due to the rise of disordered carbon, as revealed in Figure 5b. Although high pyrolysis temperature leads to the formation of more disordered carbon, it also results in the decreased carbon interlayer distance in graphite-like nanocrystals, which adversely affects the K-ion bulk insertion due to the large size of K ions [42]. As a result, M1000 exhibits a more negligible bulk-insertion contribution than M700 at high current densities (Figure 13d).



Figure 14 Proposed K-ion storage mechanisms in L700 (a), M700 (b), and H700 (c).

Based on the above results, we propose lignin molecular weight's role in the LHCs and their corresponding K-ion storage mechanisms in PIBs. The K-ion storage capacity in LHCs depends

on the bulk-insertion and surface-adsorption sites available in HCs, which are, in turn, determined by pyrolysis conditions and lignin precursors (molecular weight). Bulk-insertion of K ions occurs in the graphite-like nanocrystals with considerable interlayer space in the HCs. In contrast, surface-adsorption of K ions happens mainly in disordered carbon regions in the HCs. Under the same pyrolysis temperature (*e.g.*, 700 °C), low-MW lignin tends to produce more graphite-like nanocrystals because it is easier to get depolymerized, fragmented, and graphitized. However, LHCs from low-MW lignin possess the least disordered carbon and thus have the most negligible surface-adsorption K ions (**Figure 14**a), resulting in limited total K-ion storage capacity in L700.

In contrast, high-MW lignin tends to lead to a more disordered carbon structure due to its highlevel difficulty in depolymerization, fragmentation, and amortization. The disordered carbon would contribute to the K-ion storage *via* the surface-adsorption mechanism (Figure 14c). On the other hand, H700 has the least graphite-like nanocrystals with suitable carbon interlayer distance, leading to limited contribution from K-ion bulk-insertion and electronic conductivity. LHCs derived from medium-MW lignin (M700) possess balanced disordered carbon and graphite-like nanocrystals with a considerable interlayer distance, which lead to overall high K-ion storage capacity through the combined surface-adsorption and bulk-insertion (Figure 14b).

From the above results, it can also be found that the pyrolysis temperature has two-fold functions in determining the carbon structure of LHCs and the K-ion storage mechanism. First, pyrolysis temperature helps form disordered carbon from the depolymerization, fragmentation, and amortization from lignin precursors and the rearrangement of disordered carbon into graphite-like nanocrystals. The formation of disordered carbon occurs at relatively low pyrolysis temperatures and accounts for increased K-ion storage capacities for LHCs derived from 500–700 °C. Secondly, the rearrangement of disordered carbon into graphite-like nanocrystals happens at all temperatures but is much accelerated at higher pyrolysis temperatures (such as 1000 °C), resulting in decreased carbon interlayer distance and reduced K-ion bulk-insertion. The

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formation of disordered carbon and graphite-like nanocrystals in LHCs derived from lignin is a competing process as the pyrolysis temperatures increases. The optimal pyrolysis temperature (700 °C in this thesis) would lead to the balanced amount of disordered carbon and graphite-like nanocrystals with large interlayer distances to achieve maximum K-ion storage performance *via* both surface-adsorption and bulk-insertion mechanisms.

It is expected that the finding made in this thesis would be inspirable for HC anodes in beyond-LIBs, such as SIBs and PIBs. For the first time, this thesis unravels the importance and working mechanism of lignin molecular weight in determining the K-ion storage performance of HCs, which has been neglected in previous studies. It is discovered that, in addition to the traditionally recognized pyrolysis temperature, the structure of biomass precursors (such as molecular weight) needs to be carefully controlled and optimized to obtain reproducible and optimal electrochemical performance for alkali-ion storage *via* bulk-insertion and surface-adsorption mechanisms.

Chapter 4: Roles of Electrolyte Chemistry in Lignin-derived Carbon anodes

LHCs as popular anode materials for practical PIBs were studied due to their high K-ion storage and relatively low material cost. However, the role of electrolyte chemistry in determining LHC performance and K-ion storage mechanism has been rarely investigated. Herein, we selected the best-performed M700 as the anode and systematically studied the influence of four electrolyte systems, *i.e.*, two K salts (KPF₆ and KFSI) in carbonate ester and ether solvents, on the K-ion mobility, cycling stability, and charge transfer kinetics on LHC anode in PIBs. It is found that M700 achieved the best cycling stability and kinetics performance in the KFSI EC/DEC electrolyte. Mechanimsic study disclosed that the improved performance could be ascribed to the formation of robust KF-rich SEI resulting from FSI⁻ decomposition, which effectively prevented irreversible side reactions and severe structural decay (*e.g.*, exfoliation and pulverization). The degradation mechanisms of other electrolyte systems are also explained from the viewpoints of SEI formation and solvation/desolvation effect. It is expected that this thesis will provide guidance on the anode and electrolyte selection and design for PIBs in the near future.

4.1 Material Structure

The morphology and structure of M700 are presented in **Figure 15**. M700's XRD pattern in Figure 15a displays two broad peaks centered at 22.0° and 43.1°, which are assigned to the (002) and (010) planes of graphite (JCPDS PDF No. 08–0415), respectively. According to Bragg's law ($\lambda = 2d\sin\theta$) ¹⁷, The *d*-spacing of M700 is estimated as 4.04 Å, which could be beneficial for hosting large-sized K ions. The broad peaks indicate the disorder and deficiencies in the typical hard carbon structure. Raman spectrum (Fig. 15b) shows two summits located at 1331 and 1595 cm⁻¹ which are related to the D-band and G-band, respectively. Studies indicated that the intensity of D-band could evaluate the degree of sp³ sufficiency in diamond-like carbon materials ¹⁸, representing heterogeneity and defects in the near-surface region. In contrast, the G-band represents sp² vibration in graphite-like materials and reflects homogeneity. In this thesis, M700's

ratio of D-band and G-band's intensity (I_D / I_G) is calculated to be 0.88, indicating defective incoherence on a large scale. These defects might provide sufficient absorption energy for the surface-driven storage of K ions ¹⁹.



Figure 15 XRD (a), Raman spectrum (b), SEM images (c-e), TEM (f-g), and HRTEM (h) of ligninderived hard carbon.

SEM images in Figure 15c-e illustrate the morphology of M700 microparticles sizing from ~70-160 µm. Previous studies indicated that the porosity was created from the 'fragmentation' period during the pyrolysis process ²⁰. The reactions of functional groups and covalent bonds in lignin emitted VOCs and left sufficient porous structures in carbon ²¹. TEM images in Figure 15f-g disclose that the carbon nanospheres with diameters from 33-65 nm agglomerate into secondary particles (Figure 15c-e). The carbon nanospheres bring in sufficient surface deficiencies, which create energy for accommodating K ions *via* surface adsorption. In the HRTEM image (Figure 15h), M700 exhibits a typical hard carbon structure, *i.e.*, house of cards, in which graphite-like layered nanocrystals with spherical shapes land on the amorphous background in an overlapped manner. The interplanar distance of the layered area is measured as 3.72, 3.88, and 4.16 Å in different regions (Figure 15h), which are more extensive than that of graphite (3.35 Å) and consistent with the XRD calculation (4.04 Å). The two diffraction rings in the SAED pattern (inset in Figure 15h) correspond to the (002) and (101) plane of M700 nanocrystals.

4.2 Electrochemical Performance

Cyclic voltammetry (CV) measurement was performed to investigate the charge storage behaviors of M700 anodes in these four electrolytes. EC/DEC, as the most studied solvent combination, has a wide stability window, which brings fewer interfacial side reactions between the M700 anodes and the electrolytes ²². EC with high polarity and high dielectric constant contributes to the SEI formation and K-ion solvation, while DEC with low viscosity benefits the K-ion mobility. DME, as a linear ester solvent, is born with excellent diffusivity ²³. The K salts in the electrolytes participate in SEI formation and electronegativity adjustment.

As shown in **Figure 16**, LHC shows very similar CV profiles with two pairs of redox peaks at 0.93-1.02 / 0.60-0.65 V (O/R) and 0.42-0.49 / 0.01 V, respectively, in KPF₆ EC/DEC, KFSI EC/DEC, and KFSI DME. However, the CV profiles of M700 in KPF₆ DME (Figure 16c) present more redox peaks at very different peak positions, indicating more side reactions and a unique K-

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ion storage mechanism. Besides the two pairs of O/R peaks at 0.74 / 0.90 V and 0.24 / 0.01–0.23V, an additional oxidation peak is found at 2.74 V and could be ascribed to the oxidative decomposition of DME solvent at high voltages ²⁴. This peak also appears in the 2nd and 3rd cycles, indicating the continuous decomposition of DME. This constant decomposition causes the rapid consumption of electrolytes in K//M700 half cells.



Figure 16 CV profiles of K//LHC half cells with 0.8 M KPF6 EC/DEC (a), 1.0 M KFSI EC/DEC (b), 1.0 M KPF6 DME (c), and 1.0 M KFSI DME (d) as the electrolytes.

After disassembling the K//M700 cell after 5 cycles, we find that the electrolyte almost dries out, and the electrode cracks (as marked in white dash lines and red circles in **Figure 17**), suggesting the exfoliation and pulverization of M700. Moreover, it is found that LHC suffers from severe capacity degradation in 1.0 M KPF₆ in DME, as discussed later on. Due to the limited

electrochemical window of DME, more side reactions are involved during the C/D process in the K//M700 cell with 1.0 M KPF₆ in DME. These side reactions continuously consume the solvents and produce gas residues to the battery system, such as H_2 , CO₂, CO, bringing new safety issues $^{25, 26}$.



Figure 17 SEM images of LHC electrodes before cycling (a, b) and after 5 cycles at 0.8 M KPF6 in EC/DEC (c), 1.0 M KFSI in EC/DEC (d), 1.0 M KPF6 in DME (e), and 1.0 M KFSI in DME electrolytes

(f).

Moreover, it is noticeable that the 1st half cycle of CV profiles witnessed the least and the most area of irreversible peaks in KPF₆ DME and KFSI DME, respectively. The irreversible peaks in the 1st half cycle of discharging reflect the capacity contributing to the SEI formation. During this process, FSI⁻, EC, and DEC decompose into KF, (CH₂OCOOK)₂, and C₂H₅COOK, respectively

²⁷. A functioning SEI with stability and elasticity can effectively prevent the M700 anode from electrolyte corrosion, transfer K ions at high rates, and prevent irreversible volume damage. Ideally, once a firm SEI is formed in the 1st cycle, the chemical reaction between the electrode and the electrolyte will stop. Afterward, only electrochemical reactions will continuously contribute to K-ion storage capacity until the complete deactivation of the electrode materials.

The cycling stability and rate performance of M700 in these four electrolytes are compared in **Figure 18**. As shown in Figure 18a, M700 in 1.0 M KFSI EC/DEC exhibits excellent cycling stability at 100 mA g⁻¹ and realizes a high specific capacity of ~200 mAh g⁻¹ with a minimal capacity degradation of 1.28 ‰ per cycle. After 550 cycles, the specific capacity maintains at 103 mAh g⁻¹. The Coulombic efficiency (CE) of the M700 anode in this electrolyte is 98.8% during the initial 50 cycles and exceeds 99% after the 19th cycle. In 1.0 M KPF₆EC/DEC and 1.0 M KFSI DME, M700 achieves a decent initial capacity but experiences a severe capacity degradation, with less than 100 mAh g⁻¹ remained after 100 cycles. M700 shows a higher specific capacity is maintained for M700 in KPF₆ DME than in KPF₆EC/DEC. The worst cycling stability is observed for M700 in 1.0 M KPF₆ DME. M700 suffers from the most rapid capacity degradation, and the cell dies after 40 cycles.

Figure 18b presented the irreversible capacity loss of M700, the difference between charging and discharging capacities during the 1st cycle, in the four electrolytes. It is observed that M700 in KPF₆ DME experiences the least irreversible capacity loss (23.8%) during the 1st discharging process. This result matches the irreversible capacity corresponding to the irreversible peaks in CV curves, contributing to the SEI formation on the anode ²⁸. In the KPF₆ DME electrolyte, M700 has minimal irreversible reactions and does not have delicate SEI to separate it from liquid electrolytes. As a result, uncontrollable interfacial side reactions cause damage to active materials and consume the electrolytes continuously, resulting in inferior cycling performance.

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Figure 18 Cycling performance of lignin-derived carbon in four electrolytes (a) at 100 mA g⁻¹; 1st cycle capacity decay (b) Coulombic efficiency (c) of M700 in four electrolytes. Rate performance of LHC in four electrolytes (d) and C/D profiles of LHC in 1.0 M KFSI in EC/DEC at different rates (e).

In contrast, carbonate-based electrolytes often form a relatively thick SEI layer at low potentials due to the strong reducibility of K metal ²⁴. As shown in Figure 18c, KPF₆ EC/DEC achieves the lowest CE among these four electrolytes in each cycle after the 2nd cycle, indicating the continuous mild electrolyte decomposition and repeatable SEI damage/reconstruction. In KFSI EC/DEC, the CE exceeds 99% in the 19th cycle and has maintained the highest among the four electrolytes since then, indicating a firm and functioning SEI derived mainly from FSI⁻ decomposition. Technically, M700 in KPF₆ DME should suffer from low CE during cycling tests because of excessive side reactions. However, the oxidative decomposition of DME solvent at high potentials in the charging process compensates for the reductive capacity loss for SEI formation so that the capacity difference between the charging and discharging process is minimal. Despite the instability of ether-based electrolytes at high potentials, KFSI DME achieves much-enhanced cycling stability, which again fortified the favourability of KFSI in effective SEI formation even in DME solvent.

M700 in 1.0 M KFSI EC/DEC at higher current densities also maintains the highest capacity (70.3% and 54.3% at 200 and 500 mA g⁻¹, respectively) and recovers 98.9% of its initial capacity when the current density is reversed back to 50 mA g⁻¹ (Figure 18d). In comparison, the capacity retention of M700 at 500 mA g⁻¹ are 45.3%, 54.3%, 0%, and 29.5% in 0.8 M KPF₆ EC/DEC, 1.0 M KFSI EC/DEC, 1.0 M KFSI EC/DEC, 1.0 M KFSI DME, and 1.0 M KFSI DME, respectively. M700 in KFSI EC/DEC maintains the highest capacity at high rates and exhibits the best rate performance. K ions have the weakest solvation structure with EC solvents as K⁺(EC)₂ than Li ions and Na ions ¹³. Considering FSI- also contributes to the SEI formation, there are sufficient EC solvents left for K-ion solvation in the KFSI EC/DEC electrolyte. The relatively low desolvation energy of K ions benefits their fast ionic transport in this electrolyte, leading to good rate performance of M700.

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4.3 Kinetics Analysis

EIS measurement was performed to examine the influence of electrolytes on internal resistance and SEI formation in the LHC anode. **Figure 19**a-d shows the EIS profiles of K//M700 half cells at the charging state with these four electrolytes. By applying an equivalent circuit model (inset in Figure 19e), three resistances can be calculated, including R_s , R_f , R_{ct} . It is noticeable that R_s contains a minimal portion in the total resistance ($R = R_s + R_f + R_{ct}$), and the resistance difference among batteries with different electrolytes mainly lands on the R_f and R_{ct} . Figure 19e shows that K//M700 half cells with KFSI-based electrolytes experience a remarkable R_{ct} drop after SEI formation at the 1st cycle, indicating that their SEI effectively improves the charge exchange kinetics by allowing K ions to transfer through SEI and react at the interface between the electrode and the SEI. Their R_f and R_{ct} remain relatively stable in the following cycles, suggesting SEI's stability without evident damage and reconstruction.

However, KPF₆-based electrolytes do not contribute to such functioning SEI layers. The R_f after the 1st cycle indicates the SEI formation in KPF₆ EC/DEC, but this SEI malfunctions in promoting the ionic transfer and charge exchange because the R_{ct} significantly surges from ~1–7 k Ω . Also, the R_f of K//M700 half cells in KFSI EC/DEC is considerably smaller than that in KPF₆ EC/DEC, indicating the higher electronic conductivity of KFSI-contributed SEI. Previous studies reported that the solvation energy of KFSI-based electrolytes was higher than that of KPF₆-based ones. In this way, KFSI-based electrolytes can further prevent excessive side reactions between K ions and the SEI by solvating more K ions with organic molecules ²⁹. Therefore, from the viewpoint of resistance, K salts significantly affect SEI layers' functionality. In this thesis, only KFSI-based electrolytes contribute to effective and stable SEI products. In terms of KPF₆ DME, the R_f and R_{ct} are neglectable in the first two cycles, indicating nearly no SEI formation in the beginning. On the one hand, this result means the impeccable ionic mobility in both diffusion and charge transfer process at the initial cycles. On the other hand, without the SEI functioning as ionic transferring channels, solvated K ions with such a considerable size directly intercalate into the M700 anode, leading to pulverization of active materials (Figure 17) and severe capacity degradation (Figure 18a).



Figure 19 EIS results for K//M700 cells with electrolytes of KPF₆ EC/DEC (a), KFSI EC/DEC (b), KPF₆ DME (c), and KFSI DME (d) at fully-charged state at the initial and 1st, 2nd, 5th, and 20th cycles; modeling results of R_s, R_f, and R_{ct} for each electrolyte (e) with the equivalent circuit embedded.

After analyzing the stability and functionality of SEI layers, the GITT technique was then introduced to study the diffusivity difference of K ions in these four electrolytes (**Figure 20**a-b). The diffusion co-efficiencies of K ions can be calculated from **Equation 3**:

$$D_{K^{+}} = \frac{4}{\pi} \left(\frac{m_{B}V_{M}}{M_{B}S}\right)^{2} \left(\frac{\Delta E_{S}}{\tau\left(\frac{dE_{\tau}}{d\sqrt{\tau}}\right)}\right)^{2} \approx \frac{4}{\pi\tau} \left(\frac{m_{B}V_{M}}{M_{B}S}\right)^{2} \left(\frac{\Delta E_{S}}{\Delta E_{\tau}}\right)^{2}, \left(\tau < <\frac{L^{2}}{D_{K^{+}}}\right)$$
(3)

Where m_B is the mass (~0.0001 g), M_B is the molecular weight of carbon (12.01 g·mol⁻¹), V_M is the molar volume of hard carbon (42.74 cm³·mol⁻¹), S is the effective area of the electrode (1.13 cm²). dE $\tau/d\tau$ is the slope of the linearized proportional of the E τ during the deposition process of duration time τ (s); \triangle Es is the potential change after every equilibrium process, L is the thickness of the electrodes ³⁰.

It is found that the K-ion diffusivity is more dependent on the solvents than K salts of electrolytes. As shown in Figure 20b, K//LHC half cells in DME-based electrolytes exhibit higher diffusion co-efficiencies than in carbonate-based ones, ascribing to the sizes of solvated K ions and the viscosity of the solvents ²³. Due to the intense polarization and high dielectric constant of EC molecules, carbonate-based electrolytes often have high viscosity and low diffusivity. Also, the ionic conductivity presents the ionic mobility in different electrolytes, which is found to be 7.5, 10.75, 8, and 13.5 mS cm⁻¹ in 0.8 M KPF₆ EC/DEC, 1.0 M KFSI EC/DEC, 1.0 M KPF₆ DME, and 1.0 M KFSI DME, respectively ^{31, 32}. Studies indicated that the Stokes' radius of the K⁺-DME chelation was smaller than K⁺-EC/DEC after solvation ³³. Therefore, it is understandable that K ions in DME with a smaller size diffuse faster than in EC/DEC.



Figure 20 GITT (a), $D_{K^{+}}$ (b) of K//M700 half cells with the four electrolytes; RSCV profiles (c) of M700 in KFSI EC/DEC and b-value results by voltage (d) for K ions in four electrolytes; K-ion storage behavior analysis (e) and capacity contribution ratio results (f) in four electrolytes.



Figure 21 VSCV profiles of K//LHC half cells with 0.8 M KPF6 in EC/DEC (a), 1.0 M KFSI in EC/DEC (b), 1.0 M KPF6 in DME (c), and 1.0 M KFSI in DME electrolytes (d).

Moreover, RSCV (Figure 20c, **Figure 21**) was measured to calculate the *b*-value at different potentials in both the charging and discharging process (Figure 20d, **Figure 22**) to explain the K-ion storage behaviors in M700 with different electrolytes. It is worth noting that the *b*-value indicates the K-ion storage behaviors of either bulk insertion or surface adsorption and their corresponding voltage window. A quantitative analysis method for hard carbon materials, indicated by Yang Xu³⁴, was applied in this thesis. According to the power-law relationship, the peak current *versus* the scanning rate in the CV profile follow **Equation 4**:

$$i = av^b \tag{4}$$

Where *i* is peak current, *v* is scan rate, a and b are adjustable constants.



Figure 22 Calculation of b-value of K-ions at 0.8 M KPF6 in EC/DEC (a), 1.0 M KFSI in EC/DEC (b), 1.0 M KPF6 in DME (c), and 1.0 M KFSI in DME electrolytes (d).

By plotting log(*i*) against log(*v*), the *b*-value can be extracted from the slope in the linear area (<1 mV s⁻¹), as shown in Figure 5d. Theoretically, b-value (0.5–1.0) shows the dominance of two K-ion storage behaviors: when *b*-value = 0.5, K-ion storage is fully contributed by diffusion-controlled faradic bulk-insertion; when *b*-value = 1.0, the capacity is entirely dominated by capacitance-controlled surface-adsorption originated from electrochemical reactions. In this thesis, during the discharging of K//M700 half cells with four electrolytes, K ions are harvested by the M700 electrodes sequentially *via* surface-adsorption, bulk-insertion, and surface-adsorption

in the voltage window of 2.0–3.0 V, 0.5–2.0 V, and 0.01–0.5 V, respectively. While in the charging process, K ions are released reversely *via* surface-adsorption, bulk-insertion, and surface-adsorption at 0.01–0.25 V, 0.25–0.75 V, 0.75–3.0 V, respectively.

After determining the leading K-ion storage behaviors at each potential, it is vital to study the total charge harvested/released at the whole voltage window of 0.01-3 V *via* each behavior. Trasatti's method was used to quantify these two contributions (**Equation 5**)³⁵:

$$Q(v) = Q_s + Q_b = Q_s + kv^{-\frac{1}{2}}$$
(5)

Where *v* is scan rate, *k* is adjustable constants. M700 provides reversible K-ion storage capacity (Q) roughly in two steps: bulk-insertion (Q_b) and surface-adsorption (Q_s); the bulk insertion occurs in graphite nanocrystals and the K-ion adsorption occurs in near-surface amorphous deficiencies. The total charge change during cycling at different scanning rates is shown in **Figure 23**.



Figure 23 Electric charge changes during C/D at 0.8 M KPF₆ in EC/DEC (c), 1.0 M KFSI in EC/DEC (d), 1.0 M KPF₆ in DME (e), and 1.0 M KFSI in DME electrolytes (f) at scanning rates of 0.1–50 mV s⁻¹.

After plotting Q and $v^{1/2}$, as shown in Figure 20e, the slope is the *k*, and the interception is the Q_s . By determining *k* and Q_s , the ratio of the two K-ion storage behaviors can be calculated (Figure 5f). Generally, as the scanning rate increases, the bulk-insertion percentage continuously

decreases, ascribing to the long diffusion path of K ions in bulk-insertion. More importantly, at the scanning rate of 0.3 mV s⁻¹, the most suitable rate to explain the electrochemistry of galvanostatic C/D process at 100 mA g⁻¹, the surface-adsorption ratios of total K-ion storage capacity are 63%, 63%, 38%, and 57% in 0.8 M KPF₆ EC/DEC, 1.0 M KFSI EC/DEC, 1.0 M KPF₆ DME, and 1.0 M KFSI DME, respectively. This result also matches with the EIS conclusions that SEI is not well-formed in KPF₆ DME electrolyte. Without a reliable SEI, the layered structures in M700 are easily expanded in the C/D process so that a higher portion of bulk insertion contributed to the total K-ion storage capacity in KPF₆ DME.

4.4 Degradation Mechanism Analysis

It is essential to understand that the functionality of SEI in different electrolytes determined by the activity of the solvents and the stability of the SEI chemistries. XPS was employed to examine the chemical compositions of the SEI produced on the M700 anode in different electrolytes. **Figure 24**a presents the contents of SEI species fitting from C1s, O1s, and F1s spectra. In the C1s spectra, K_2CO_3 , RCOOK, C-O, C-C, C-H peaks are all observed in four samples. K_2CO_3 and RCOOK are mainly from carbonate decomposition, while the C-O-C content is from ether-based solvents. C-C and C-H both refer to the sp²-C content in the SEI layer. For the O1s spectra, all samples exhibit the C-O, C=O, and K salt peaks. However, RO-COOK only shows in carbonatebased electrolytes, and R-OK is present only in ether-based electrolytes. In terms of the F1s spectra, the SEI in KPF₆-based electrolytes contains K_xPF_y , $K_xPO_yF_z$, and two K-F peaks, while the SEI from KFSI-based electrolytes contains -SO_xF and two K-F peaks. Figure 24b gives the full XPS spectra for M700 in four electrolytes at the fully charged state at the 5th cycle.

Figure 24c compares the content ratio of each SEI species. SEI from KFSI-based electrolytes shows high inorganic KF content, while SEI from KFP₆-based ones contains a high portion of organic compounds. Li et al. reported SEI formation mechanism in KFSI-based electrolytes by calculating the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular

orbital (LUMO) of the FSI-, EC, DEC, and DME *via* density functional theory (DFT) ²⁷. From the LUMO energy level viewpoint, the decomposition order for SEI formation should be FSI-, EC, DEC, DME, PF6- (KPF6 has the highest LUMO energy level inorganic salt). In detail, due to the lower LUMO energy level of FSI⁻ than DME, FSI⁻ decomposition leads the SEI formation with the highest KF content ratio in KFSI DME.

Similarly, the LUMO energy level of FSI⁻ is slightly lower than EC and DEC in KFSI EC/DEC electrolyte, so that FSI⁻ still contributes most in the SEI formation. On the contrary, in KPF₆-based electrolytes, the solvents get reduced first, forming an unstable organic-leading SEI ³⁶. This result also matches the R_f of K//M700 half cells in four electrolytes (Figure 19e), where KFSI EC/DEC contributes to the thinnest SEI.



Figure 24 XPS peak fitting results (a) with full-scale XPS patterns (b) and SEI species ratio (c).

Considering the EIS results, the relative stability of the KFSI-based electrolyte system can be inclusively ascribed to the following reasons. 1) The high-KF SEI effectively separates the M700 anode with the organic solvents, preventing further deterioration such as pulverization and carbon-layer exfoliation. 2) The high solvation energy of KFSI-based electrolytes guarantees the sufficiency of K-ion solvation with the organic molecules, preventing irreversible corrosion of bare K ions to the SEI film. Instead, KPF₆-based electrolytes are more reactive and occur a high-organic-compound SEI, with which the anode still slowly reacts with the electrolytes, and the bare K ions keep corrode the SEI, triggering the low CE and more evident capacity degradation.

HRTEM and SAED techniques were employed to characterize the structural difference of cycled electrodes in terms of the SEI thickness, interlayer distance, and graphitization degree. As shown in **Figure 25**, the M700 anode is protected by the thickest SEI in KPF₆ EC/DEC, followed by KFSI EC/DEC and KFSI DME. In the KFP₆ DME electrolyte, nearly no SEI formation is observed. As aforementioned in XPS analysis, the SEI chemistry in KPF₆ EC/DEC electrolyte in Figure 25a is mainly organic molecules, such as (CH₂OCOOK)₂ from EC decomposition. EC plays a vital role in SEI formation and K-ion solvation in this system, while DEC benefits K-ion diffusion with linear molecular structure and smaller viscosity. In KFSI EC/DEC electrolytes (Figure 25b), most of the SEI chemistry should be KF from FSI⁻ decomposition, followed by (CH₂OCOOK)₂, C₂H₅COOK from EC, DEC decomposition, respectively. While in KFSI DME (Figure 25d), only FSI⁻ contributes to the SEI with a higher KF ratio, which matches the XPS results in Figure 6c.

Similarly, the scarcity of SEI in KPF₆ DME is due to the relatively high LUMO energy levels, both DME and PF_6^- barely contributing to the SEI formation (Figure 25c). SEI plays a vital role in stabilizing the batteries by separating the electrolyte and electrode. A firm and elastic SEI can effectively constrain the volume change in the C/D process, preventing the anode from deactivation (*e.g.*, exfoliation, pulverization) and severe capacity decay.

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Moreover, the interlayer distance in typical selected areas of cycled LHC anodes was measured in Figure 25. In KPF₆ EC/DEC, M700 maintains the smallest average interlayer distance of 3.42– 4.36 Å and the biggest graphite-like nanocrystals (Figure 25a). The bright and sharp diffraction rings in their SAED patterns also suggest the higher graphitization degree ³⁷. Therefore, in KPF₆ EC/DEC, LHC keeps the most layered structure, indicating that only K ions pass the ionic conducting channels in EC-contributed SEI with a high organic compounds ratio instead of K⁺(EC)₂ chelation co-intercalation. On the contrary, M700 in KPF₆ DME with negligible SEI exhibits the most significant interlayer distance, probably due to the K⁺(DME)₄ co-intercalation mechanism, similar to graphite reported by Wang *et al.* ¹⁶. The SAED patterns of M700 after cycling at KFSI-based electrolyte with nebulous rings indicate the growth of amorphous structures and disorder deficiencies. The interlayer distance of the graphite-like nanocrystal units in M700 increases in the two KFSI-based electrolytes compared to KPF₆ EC/DEC because smaller ordered structures tend to entropy increase, which, to an extreme extent, could be exfoliated. However, with the effective KF-leading SEI constraining the M700 anode, the volume change can only be achieved in a limited range, lessening the capacity decay in long cycling tests.



Figure 26 K-ion storage and capacity degradation mechanism in the four electrolytes.

It is vital to understand the electrolyte functionality in aspects of SEI formation and ionic diffusion so that PIBs can be optimized at a more delicate level. **Figure 26** summarizes the solvation effects, SEI formation, K-ion storage mechanism, and current issues of the four electrolyte systems. KFSI EC/DEC realizes excellent electrochemical performance due to the following reasons. 1). The KF-leading SEI with excellent elasticity and stability from FSI decomposition can effectively separate the M700 anode from the electrolytes, which prevents excessive side reactions, alleviates the volume change, and ameliorates the cycling stability. 2). FSI decomposes before EC to generate the SEI so that K ions have sufficient EC to complete the solvation; solvated K ions can realize the charge transfer around the SEI mildly, preventing the SEI corrosion. Also, the solvation effect can reduce side reactions, regulate polarization, ameliorate KFSI corrosion to the current collector. 3). Ring-shaped EC molecules have stronger

polarity and higher viscosity than linear DME, preventing excessive solvent diffusion in the anode after desolvation at SEI and preserves enough accommodation space for the K ions so that M700 in KFSI EC/DEC electrolyte maintains a relatively high capacity.

Chapter 5: Conclusions and Perspectives

5.1 Contributions of this work

LHC material was fabricated from low, medium, and high-MW lignin at serial PTs. The synergy of pyrolysis conditions and lignin MW on the LHC products was thoroughly discussed in terms of morphology, carbon structure, electrochemistry, kinetics, and K-ion storage mechanisms. Medium and high-MW LHCs exhibited porous structures, while low-MW lignin generated mirror-like LHC without noticeable pores. Among all LHCs, M700 (9600 g/mol @700 °C) exhibited the best electrochemical performance: a reversible specific capacity of ~300 mAh g⁻¹, good cycling stability of 79% retention after 100 cycles, and excellent rate performance of 69% retention at 200 mA g⁻¹. M700 also showed the most significant interplanar distance and the highest specific surface area, contributing to 42% of K-ion storage in bulk insertion and 58% in surface adsorption. From the standpoint of practical battery application, M700 should meet essential requirements to be considered as promising PIB anodes, including an optimal mixture of amorphous structure and graphite-like nanocrystals with a considerable interplanar distance, high and stable electrochemical performance, and good reaction kinetics. The ideal HC structure for K-ion storage could be achieved by carefully selecting biomass precursors (molecular weight) and controlling pyrolysis conditions.

After investigating the electrolyte effect on M700 anode in PIBs using four common electrolytes, we explained the differences in electrochemical performance from aspects of SEI formation, Kion storage behaviors, solvated K-ion mobility, and battery degradation mechanisms. KFSI EC/DEC contributed to sufficient K-ion solvation and high-KF SEI formation, which prevented SEI corrosion and greatly enhanced the cycling stability and rate capability of the M700 anode. KFSI EC/DEC electrolyte led to a minimal capacity degradation of 1.28 ‰ per cycle and a high reversible specific capacity of ~200 mAh g⁻¹ at 100 mA g⁻¹. It is expected that this thesis sheds

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light on electrolyte multifunctionality in PIBs and provides systematic evaluation methodologies for electrolyte research shortly.

5.2 Limitations of this work

The development of PIBs is still at an early stage. Different from LIBs, the conventional graphite anodes do not present superiority in PIBs. At present, most studies on HC anodes are conducted to explore their specific capacity and cycling stability. Because of the large ionic radii of K ions bringing in differences in intercalation capacity, KC_x stage structures, voltage profiles, and cycling lifespan, the electrochemical performances of HC anodes in PIBs are usually not as competitive as in LIBs and SIBs.

5.3 Future recommendations

- From the viewpoint of fine synthesis, techniques such as plasma-enhanced atomic layered deposition (PEALD) should be used in the future to magnify the HC performance.
- Also, it is vital to evaluate HC compatibility with the electrolyte, the thermal stability, the volume expansion, the rate performance, and the high/low-temperature performances.
- It is always challenging to obtain practical full cell strategies for PIBs, considering the insufficient theoretical studies such as SEI formation and K-ion storage simulation in HC.
- In order to achieve this, theoretical research, including DFT calculations in PIBs, is suggested.
- Meanwhile, novel electrolytes and binders specifically for PIBs have seldomly been studied and are future research directions.

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