SUB-MICRON PITCH VARIABLE DIFFRACTION GRATING USING NANOPOROUS ELECTRODES AND ELECTROPHORESIS OF DYE IONS

by

RICHARD TIK FAI WONG

B.A.Sc.H., University of Waterloo, 2006

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Engineering Physics)

THE UNIVERSITY OF BRITISH COLUMBIA (VANCOUVER)

AUGUST 2009

© Richard Tik Fai Wong, 2009

ABSTRACT

One approach to achieve non-mechanical beam steering is to use variable diffraction devices, whose intensity and direction of the outgoing diffractive orders can be actively (typically electronically) altered by modifying the optical properties of the device. Devices with submicron features are of particular interest when working with visible wavelengths, since such gratings can, when not activated, produce only an undeflected beam as the output and, when activated, produce diffractive orders at large deflection angles that appear and disappear entirely. Such sub-micron pitch variable diffraction gratings can be achieved by electrophoretically moving dye ions into and out of appropriately patterned transparent electrically-conductive nanoporous electrodes. This study aimed to explore their potential for use in practical devices.

One significant technical hurdle associated with these devices has been the irreversible electrochemical reactions that can be induced with an applied voltage difference between the two electrodes exceeding a critical value on the order of 1 V. These reactions are undesirable as they limit the lifetime of the device. However, it was observed that when operating within such a voltage limit the optical response time is undesirably long - on the order of seconds. To better optimize the lifetime and response time of these devices, an electron tunneling model of the electrochemical reaction threshold was developed and verified. This enabled the use of a high speed drive circuit that was able to improve the response time by a factor of 50 without compromising the lifetime of the device.

A prototype grating with nanoporous zinc antimonate electrodes and methylene blue dye-methanol solution was fabricated using focused ion beam milling. Modulation of a diffractive order was observed with this prototype, where the exit beam geometry was in good agreement with the model. The diffractive efficiency of the diffractive order was observed to be 3.9×10^{-3} when in the charged state and 7.9×10^{-4} when in the uncharged state with an optical switching time of 250 ms. These observations demonstrated the potential of this type of device to achieve large angular deflection and fast operating speed for non-mechanical beam steering applications.

TABLE OF CONTENTS

A	BSTR	АСТ	ii
Т	ABLE	OF CONTENTS	iii
L	IST O	F TABLES	vi
L	IST O	F FIGURES	vii
A	CKNC	WLEDGEMENTS	xi
1	INT	RODUCTION	1
2	BA	CKGROUND	7
	2.1	COMPLEX INDEX OF REFRACTION	7
	2.2	EFFECTIVE MEDIUM THEORIES	10
	2.3	DIFFRACTION GRATING	
	2.4	TOTAL INTERNAL REFLECTION	
	2.5	ELECTRIC DOUBLE LAYER	17
	2.6	Electrophoresis	
3	EL	ECTROPHORETIC IONIC OPTICAL DEVICES	24
	3.1	WORKING PRINCIPLE OF ELECTROPHORETIC IONIC OPTICAL DEVICES	
	3.2	SELECTION OF MATERIAL FOR PROTOTYPE	
	3.2.	Methylene Blue Ionic Dye in Methanol Solution	
	3.2.2	2 Zinc Antimonate Transparent Nanoporous Conductive Thin Film	
4	EL	ECTROCHEMICAL LIMIT	
	4.1	ELECTRON TUNNELING MODEL OF ELECTROCHEMICAL REACTIONS	
	4.2	PREDICTIONS ARISING FROM THE ELECTRON TUNNELING MODEL	
	4.2.1 4.2.2	Accumulated Charge as Onset Indicator of Electrochemical Reactions Effect of Bulk Concentration on the Threshold Applied Voltage	

	4.2.3	Effect of Surface Roughness	47
	4.3	EXPERIMENTAL VERIFICATION OF THE ELECTRON TUNNELING MODEL	48
	4.3.1	Experimental Measurements of the Threshold Voltage and Charge	48 51
	4.3.3	Measurements of the Preferential Removal of Electrode Material	53
	4.4	DECREASING TRANSITION TIME OF ELECTROPHORETIC IONIC OPTICAL DEVICES	55
	4.4.1	High Speed Drive Circuit	56
	4.4.2	Long Term Cycling Measurements	59 62
5	OP	FICAL PROPERTIES OF PROTOTYPE MATERIALS	64
	5.1	METHYLENE BLUE DYE SOLUTION	64
	5.1.1	Complex Refractive Index Measurement Procedures	64
	5.1.2	Complex Refractive Index Measurement Results	65
	5.2	ZINC ANTIMONATE NANOPOROUS ELECTRODES	66
	5.2.1	Complex Refractive Index and Porosity Measurement Procedures	66
	5.2.2	Complex Refractive index and Porosity Measurement Results	0/
	5.3	METHYLENE BLUE DYE WITHIN ZINC ANTIMONATE NANOPOROUS ELECTRODES	68 60
	5.3.2	2 Dye Deactivation Test	72
6	VA]	RIABLE DIFFRACTION GRATINGS	76
	61	INTERDIGITATED FLECTRODES AS VARIABLE DIFFRACTION GRATINGS	76
	6.2	CHARGING BEHAVIOR OF INTERDIGITATED ELECTRODES	78
	0.2	DR ODOGED DR OTOTENE DI CTERNI	. 70
	6.3	PROPOSED PROTOTYPE PATTERN	81 81
	6.3.2	Predicted Performance of the Designed Grating	83
	6.3.3	Predicted Performance with Different Grating Thickness and Period	86
7			
	PRO	DTOTYPE GRATING FABRICATION	88
	PR (DTOTYPE GRATING FABRICATION	. . 88 88
	PRO 7.1 7.2	DTOTYPE GRATING FABRICATION Focused Ion Beam Milling Protective Chromium Coating	88 88 91
	PRO 7.1 7.2 7.3	DTOTYPE GRATING FABRICATION Focused Ion Beam Milling Protective Chromium Coating Critical Point Drying	 88 88 91 93
8	PR(7.1 7.2 7.3 DIF	DTOTYPE GRATING FABRICATION Focused Ion Beam Milling Protective Chromium Coating Critical Point Drying FRACTION PATTERN FROM A FABRICATED GRATING	88 88 91 93 . . 97
8	PRO 7.1 7.2 7.3 DIF 8.1	DTOTYPE GRATING FABRICATION Focused Ion Beam Milling Protective Chromium Coating Critical Point Drying FRACTION PATTERN FROM A FABRICATED GRATING Observed Beam Directions	88 91 93 97 98
8	PRO 7.1 7.2 7.3 DIF 8.1 8.2	DTOTYPE GRATING FABRICATION FOCUSED ION BEAM MILLING PROTECTIVE CHROMIUM COATING. CRITICAL POINT DRYING. FRACTION PATTERN FROM A FABRICATED GRATING OBSERVED BEAM DIRECTIONS OBSERVATION OF THE MODULATION OF THE -1R DIFFRACTIVE ORDER	88 91 93 97 98 98

9	CONCLUSION 102]
RF	CFERENCES 100	5
AF	PPENDIX A: GSOLVER® DIFFRACTION GRATING SIMULATION	
SC	DFTWARE PACKAGE 109)
AF	PPENDIX B: SAMPLE PREPARATION PROCEDURES FOR NANOPOROUS	
ZI	NC ANTIMONATE THIN FILMS 113	3
AF	PPENDIX C: MATLAB M-CODE USED TO PREDICT THE OUTGOING BEAM	
DI	RECTIONS	5
AF	PPENDIX D: CRITICAL POINT DRYING11'	7

LIST OF TABLES

TABLE 3.1.	MEASURED CAPACITANCE OF ELECTROCHEMICAL CELLS WITH TWO $ZNSB_2O_6$	
	NANOPOROUS ELECTRODES OF VARIOUS THICKNESSES.	.33
TABLE 5.1.	COMPLEX REFRACTIVE INDICES OF MATERIALS USED FOR MODELING THE PROTOTYP	Έ
	GRATING	.72
TABLE 6.1.	PREDICTED EXIT BEAM ANGLES FOR 0R AND -1R DIFFRACTIVE ORDERS	.86

LIST OF FIGURES

FIGURE 1.1.	SCHEMATIC REPRESENTATION OF AN ELECTROPHORETIC IONIC OPTICAL DEVICE (A)
	WITH NO APPLIED VOLTAGE, AND (B) WITH AN APPLIED CHARGE VOLTAGE
FIGURE 1.2.	SCHEMATIC REPRESENTATION OF A SUB-MICRON PITCH VARIABLE DIFFRACTION
	GRATING IN ITS (A) UNCHARGED STATE AND (B) CHARGED STATE
FIGURE 2.1.	A SIMPLE DIFFRACTION GRATING MADE FROM A MULTIPLE-SLIT ASSEMBLY, SHOWING
	THE RECONSTRUCTION OF PLANAR WAVEFRONT FOR THE 0T, 1T, AND 2T DIFFRACTIVE
	ORDERS
FIGURE 2.2.	FRUSTRATED TOTAL INTERNAL REFLECTION: (A) WITH NO MEDIUM IN THE
	EVANESCENT ZONE, TIR OCCURS AND ALL THE ENERGY GOES INTO THE REFLECTED
	BEAM. (B) WITH THE INTRODUCTION OF A HIGH INDEX MEDIUM IN THE EVANESCENT
	ZONE, TIR IS FRUSTRATED BECAUSE SOME OF THE ENERGY PROPAGATES PAST THE
	SECOND INTERFACE. (C) TIR IS FRUSTRATED BY INTRODUCING AN ABSORPTIVE
	MEDIUM IN EVANESCENT ZONE
FIGURE 2.3.	SIMPLE ELECTRICAL MODELS OF AN ELECTROCHEMICAL CELL (A) WITH NO
	ELECTROCHEMICAL REACTIONS (B) WITH ELECTROCHEMICAL REACTIONS
FIGURE 2.4.	CIRCUIT USED TO MEASURE THE OVERALL CELL CAPACITANCE OF AN
	ELECTROCHEMICAL CELL
FIGURE 3.1.	SCHEMATIC REPRESENTATION OF THE ION DISTRIBUTION AND THE SPATIAL PROFILE OF
	THE ELECTROLYTE ELECTRICAL POTENTIAL OF AN ELECTROPHORETIC IONIC OPTICAL
	DEVICE (A) WITH NO APPLIED VOLTAGE, (B) IMMEDIATELY AFTER THE APPLICATION OF
	AN APPLIED CHARGED VOLTAGE, AND (C) AFTER THE SYSTEM HAS REACHED STEADY
	STATE
FIGURE 3.2.	MOLECULAR STRUCTURE OF MB DYE
FIGURE 3.3.	ABSORPTION PROPERTIES OF MB DYE DISSOLVED IN METHANOL
FIGURE 3.4	SETUP USED TO MEASURE DISSOCIATION RATE OF AN IONIC DYE SOLUTION28
FIGURE 3.5.	A SCANNING ELECTRON MICROSCOPE IMAGE OF A CLEAVED FACE OF A TYPICAL
	NANOPOROUS $ZnSb_2O_6$ FILM
FIGURE 3.6.	(A) A SECTIONED SIDE VIEW AND (B) A SECTIONED TOP VIEW OF THE TEST CELL
	STRUCTURE
FIGURE 3.7.	A LOGARITHMIC PLOT OF A TYPICAL CHARGING CURRENT OF AN ELECTROCHEMICAL
	CELL WITH NANOPOROUS ELECTRODES OVER TIME. THE CURVATURE IN THE PLOT
	INDICATES THAT THE RELATIONSHIP IS NOT A SIMPLE EXPONENTIAL DECAY
FIGURE 3.8.	STEADY STATE CURRENT WITH INCREASING APPLIED VOLTAGE FOR A CELL COMPOSED
	OF NANOPOROUS $ZnSb_2O_6$ electrodes with different MB dye concentration.
FIGURE 4.1.	SCHEMATIC OF THE REQUIREMENTS FOR SIGNIFICANT ELECTRON TUNNELING
	THROUGH A POTENTIAL ENERGY BARRIER, THE PROBABILITY OF TUNNELING IS
	REPRESENTED BY THE SQUARE OF THE AMPLITUDE OF THE OSCILLATION OF THE
	PROBABILITY AMPLITUDE FUNCTION (ψ): (A) NO TUNNELING OCCURS BECAUSE THE
	POTENTIAL ENERGY (V) PAST THE POTENTIAL BARRIER IS GREATER THAN THE TOTAL
	ENERGY OF THE ELECTRON (E) ; (B) EVEN THOUGH THE ENERGY REQUIREMENT IS MET,
	ONLY A SMALL AMOUNT OF TUNNELING OCCURS BECAUSE THE WIDTH OF THE BARRIER
	IS TOO LARGE; (C) SIGNIFICANT TUNNELING OCCURS BECAUSE BOTH REQUIREMENTS
	ARE MET
FIGURE 4.2.	SCHEMATIC OF THE EVOLUTION OF THE RELATIVE POTENTIAL ENERGY DIFFERENCE
	(ΔV) BETWEEN THE NEGATIVE ELECTRODE (ANODE) AND CATIONS DURING THE
	REDUCTION OF THE ION WITH (A) NO ACCUMULATED CHARGE, (B) INSUFFICIENT

	CHARGE SUCH THAT THE ONLY IONS WITH STATES OF LOW ENOUGH POTENTIAL ENERGY IS TOO FAR TO GIVE SIGNIFICANT TUNNELING PROBABILITY AND (C) SUFFICIENT CHARGE TO ALLOW TUNNELING AND REDUCTION TO OCCUR. (D) TO (F)
	DESCRIBE SIMILAR STEPS FOR THE OXIDATION OF AN ANION
FIGURE 4.3.	Gaussian surface used to determine the magnitude of the electric field at different distances from the electrode. dA is taken to be much smaller
	THAN THE OVERALL EXPOSED ELECTRODE SURFACE AREA
FIGURE 4.4.	SCHEMATIC OF (A) THE POTENTIAL PROFILE AND (B) THE ION CONCENTRATION
	PROFILE FROM INSIDE THE ELECTRODE THROUGH THE ELECTRIC DOUBLE AND INTO
	THE BULK SOLUTION; THE DOTTED LINE REPRESENT THE PROFILES FOR A SYSTEM WITH
	LARGER BULK CONCENTRATION
FIGURE 4.5.	SCHEMATIC OF THE CIRCUIT FOR REAL-TIME ELECTRODE RESISTANCE MEASUREMENT. 49
FIGURE 4.6.	TYPICAL EVOLUTION OF THE ELECTRODE RESISTANCE CHANGE RATE FOR INCREASING
	RMS CELL CURRENT
FIGURE 4.7.	THE THRESHOLD RMS CELL CURRENT AT DIFFERENT APPLIED CURRENT FREQUENCIES. 51
FIGURE 4.8.	THE THRESHOLD MAXIMUM DOUBLE LAYER CAPACITIVE CHARGE AT DIFFERENT APPLIED CURRENT FREQUENCIES
FIGURE 4.9.	ELECTROCHEMICAL CURRENT FOR DIFFERENT BULK NACL SOLUTION
	CONCENTRATIONS PLOTTED AGAINST (A) THE CELL VOLTAGE AND (B) THE CELL
	VOLTAGE CORRECTED BY THE EXPECTED 59 MV/DECADE OF CONCENTRATION OFFSET. 52
FIGURE 4.10.	ATOMIC FORCE MICROSCOPE SCANS OF ANODE SURFACE FOR (A) AN UNEXPOSED
	SAMPLE, AND SAMPLES THAT HAVE BEEN ETCHED FOR (B) 0.5 HOURS, (C) 2.0 HOURS,
	(D) 17.0 HOURS
FIGURE 4.11.	THE DECREASE IN AVERAGE MEAN CURVATURE FOR POINTS OF CONVEX CURVATURE
	IN ATOMIC FORCE MICROSCOPE SCANS OF ANODE SURFACE AFTER DIFFERENT ETCH
	TIMES
FIGURE 4.12.	ELECTRICAL SCHEMATIC OF THE HIGH SPEED DRIVE CIRCUIT
FIGURE 4.13.	High speed drive circuit output cell voltage profile with a 15 V step input
	VOLTAGE
FIGURE 4.14.	OPTICAL SETUP OF TIR REFLECTANCE TEST USED TO EVALUATE THE ABSORPTION
	MODULATION IN AN ELECTRODE OF AN ELECTROPHORETIC IONIC OPTICAL DEVICE57
FIGURE 4.15.	INTENSITY MODULATION OF REFLECTED LIGHT WITH APPLICATION OF A SIMPLE 0.01
	HZ SQUARE WAVE VOLTAGE WITH VARIOUS AMPLITUDES
FIGURE 4.16.	COMPARISON OF INTENSITY MODULATION OF REFLECTED LIGHT WITH THE SIMPLE
	CIRCUIT AND THE HIGH SPEED DRIVE CIRCUIT, BOTH WITH STEADY STATE VOLTAGE OF
	0.5 V
FIGURE 4.17.	INTENSITY RESPONSE IMMEDIATELY AFTER SWITCHING TO THE ON-STATE WITH THE
T (10)	HIGH SPEED DRIVE CIRCUIT
FIGURE 4.18.	INTENSITY MODULATION OF REFLECTED LIGHT WITH APPLICATION OF 0.01 HZ SQUARE
	WAVE VOLTAGE USING THE HIGH SPEED DRIVE CIRCUIT WITH VARIOUS STEADY STATE
T	VOLTAGES
FIGURE 4.19.	EVOLUTION OVER TIME OF THE RELATIVE CHANGE IN STEADY STATE REFLECTANCE
	(CONTRAST) OF AN ELECTROPHORETIC IONIC OPTICAL DEVICE AS IT IS CYCLED AT
	U.UI HZ AI DIFFERENT STEADY STATE VOLTAGES WITH THE SIMPLE CIRCUIT AND THE
ELCURE 5 1	HIGH SPEED DRIVE CIRCUIT
FIGURE 5.1.	(A) SIDE CRUSS-SECTION AND (B) FRONT VIEW OF A TEST CELL CONTAINING A THIN
	LATER OF DIE SOLUTION FOR IKANSMITTANCE MEASUKEMENTS

FIGURE 5.2.	LOG-LOG PLOT OF THE IMAGINARY INDEX OF REFRACTION VS. MB DYE CONCENTRATION IN METHANOL SOLUTION, FITTED LINE SHOWS A TRANSFORMED
FIGURE 5.3.	LINEAR FUNCTION
	THE PREDICTED REFLECTANCE OF A LAYER WITH n_R OF 1.45 AND n_I OF 0.0020. THE
FIGURE 5.4	INCIDENT ANGLE CORRESPONDS TO θ_i IN FIGURE 4.14
FIGURE 3.4.	MEASURED REFLECTANCE OF A 800 NM THICK ZNSB ₂ O ₆ LAYER IN METHANOL COMPARED TO THE PREDICTED REFLECTANCE OF A LAYER WITH n_R OF 1.57 AND n_I
	OF 0.0032. The incident angle corresponds to θ_i in Figure 4.14
FIGURE 5.5.	IMAGINARY REFRACTIVE INDEX AS MEASURED WITHIN THE POROUS CONDUCTOR COMPARED WITH THAT EXPECTED IN THE BULK SOLUTION
FIGURE 5.6.	IMAGINARY REFRACTIVE INDEX OF THE ELECTROLYTE WITHIN THE NANOPOROUS ELECTRODE AT VARIOUS APPLIED VOLTAGES AND VARIOUS BULK CONCENTRATIONS.
FIGURE 5.7.	UPTICAL SETUP OF THE DYE DEACTIVATION TEST
FIGURE 3.8.	TRANSMITTANCE THROUGH A THIN LAYER OF DYE SOLUTION AND A NANOPOROUS THIN EILM ELECTRODE THAT IS (A) DUILLING IN DVE AND (B) DUSHING OUT DVE 75
FIGURE 6.1	A VARIABLE DIFFRACTION GRATING IMPLEMENTED AS TWO INTERDIGITATED
1 100KL 0.1.	ELECTRODES IN (A) ITS UNCHARGED STATE AND (B) ITS CHARGED STATE 76
FIGURE 6.2.	SCHEMATIC REPRESENTATION OF DIFFRACTIVE ORDERS OF A SUB-MICRON PITCH
	VARIABLE DIFFRACTION GRATING IN ITS (A) UNCHARGED STATE AND (B) CHARGED
	STATE
FIGURE 6.3.	SCHEMATIC REPRESENTATION OF ELECTRIC FIELD BETWEEN TWO FINGERS OF A SET OF IDES
FIGURE 6.4.	REFLECTANCE TEST SETUP FOR LARGE SCALE IDES
FIGURE 6.5.	REFLECTANCE ATTENUATION OF A LARGE-SCALE IDES FOR DIFFERENT APPLIED DC VOLTAGES
FIGURE 6.6.	PROPOSED PROTOTYPE GRATING DESIGN SHOWING THE DIAMOND END PATTERN, THE SHADED REGION REPRESENTS THE DYE-RICH ELECTRODE. THE GRATING LINE PERIOD IS NOT DRAWN TO SCALE
FIGURE 6.7.	DEFINITION OF ORIENTATION ANGLES IN GSOLVER®
FIGURE 6.8.	PREDICTED -1R DIFFRACTIVE EFFICIENCY MAXIMUM, EACH CONTOUR REPRESENT A
	CHANGE OF 2×10^{-4} . θ and ϕ defines the orientation in the glass slide superstrate
FIGURE 6.9.	DEFINITION OF THE ANGLES USED TO DESCRIBE THE OUTGOING BEAM DIRECTIONS85
FIGURE 6.10.	-1R DIFFRACTIVE EFFICIENCIES FOR ACTIVATED DIFFRACTION GRATING MODELS IN THEIR RESPECTIVE OPTIMAL ORIENTATION AS FUNCTIONS OF (A) THE GRATING
	THICKNESS AND (B) GRATING CHARGE PERIOD
FIGURE 7.1.	FIB MILLED IDES WITHIN NARROW GAPS BETWEEN LINES SCORED BY A DIAMOND
EICUDE 7.2	SURIBE
FIGURE 7.2.	ZNSB ₂ O ₆ SURFACE AFTER MILLING WITH A TOUPA BEAM. THE DEEP RECTANGULAR
	CROSS-SECTION 90
FIGURE 7.3.	CROSS-SECTION OF MILLED AND UNMILLED AREAS OF A NOMINALLY 1500 NM
	$ZnSb_2O_6$ sample protected with 50 nm thick protective chromium layer.
	THE PATTERN OF IDES WITH 667 NM UNCHARGED GRATING PERIOD WAS MILLED AT 300 PA
FIGURE 7.4.	CROSS-SECTION OF MILLED AND UNMILLED AREAS OF A NOMINALLY 800 NM THICK
	$ZnSb_2O_6$ sample protected with 50 nm thick protective chromium layer.

	THE PATTERN OF IDES WITH 667 NM UNCHARGED GRATING PERIOD WAS MILLED AT	Г
	300 PA	93
FIGURE 7.5.	IDES DESTROYED BY EVAPORATING FLUID DROPLETS AFTER CHROMIUM WET ETCH	. 94
FIGURE 7.6.	FABRICATED IDES WITH PROTECTIVE CHROMIUM LAYER REMOVED, SHOWING THE	
	PRESERVED NANOPOROUS STRUCTURE OF THE TOP SURFACE.	95
FIGURE 7.7.	FABRICATED 40 mm \times 100 mm prototype variable diffraction grating with	I
	THICKNESS OF 800 NM AND UNCHARGED GRATING PERIOD OF 667 NM.	96
FIGURE 8.1.	OBSERVED DIFFRACTION PATTERN OF A VARIABLE DIFFRACTION GRATING (800 NM	
	THICK, 667 NM UNCHARGED PERIOD, AND 2.00 μ M CHARGED PERIOD) WHEN IT IS (A	.)
	UNCHARGED AND (B) CHARGED TO 1 V.	. 97
FIGURE 8.2.	OPTICAL SETUP USED TO MEASURE THE DIFFRACTIVE EFFICIENCY OF THE -1R	
	DIFFRACTIVE ORDER.	98
FIGURE 8.3.	OBSERVED -1R DIFFRACTIVE EFFICIENCY WITH A 1 V SQUARE WAVE APPLIED	
	VOLTAGE	99
FIGURE 8.4.	OBSERVED -1R DIFFRACTIVE EFFICIENCY AT DIFFERENT APPLIED VOLTAGE LEVELS	
		100
FIGURE A.1	GSOLVER® INTERFACE AND GRAPHICAL REPRESENTATION OF A TYPICAL	
	RECTANGULAR GRATING USED TO SIMULATE THE FABRICATED IDES.	110
FIGURE D.1.	DIFFERENT METHODS OF DRYING REPRESENTED BY DIFFERENT PATHS FOR STATE	
	TRANSITION FROM A LIQUID STATE A TO A GAS STATE B	117

ACKNOWLEDGEMENTS

First of all, I would like to thank the people who gave me personal training for the advance equipments that were instrumental to this study: Mario Beaudoin and Alina Kulpa from the AMPEL Nanofabrication Facility, Mike Whitwick from the UBC MBE Laboratory, Li Yang from the SFU Nano-Imaging Facility, and Derrick Horne from the UBC Bioimaging Facility. I would also like to thank the directors of all the above facilities for giving me access to such wonderful resources. As well, I am grateful for the financial support provided by the Natural Science and Engineering Research Council of Canada for this project.

Big thanks go to Peter Friedel, Steven Gou, Weilai Li, Jason Radel, Allen Upward, Eri Watanabe, and all the past and present research assistants of the UBC Structure Surface Physics Laboratory, for the huge diversity of helpful suggestions and for the great lunchtime conversations, especially the random ones. In particular, I would like to extend a special thanks to Peter Hrudey, whose resourcefulness and willingness to help are qualities to which I aspire, for the invaluable guidance during the first steps of the project.

I also extend my appreciation for the guidance Andrzej Kotlicki has given me with regards to the various electrical setups throughout this study.

As well, I would like to thank Michele Mossman for the huge amount of helpful advice, and especially for the immense amount of help with putting together my first published manuscript.

Of course, I would like to express my deepest gratitude to my supervisor, Lorne Whitehead. First, you have established this unique lab setting that brings together the fundamental and the practical of which I am so fortunate to be take part. Moreover, the combination of freedom to explore and your timely advices provides a great learning environment. I have learned so much from you, in and out of research.

Last but not least, a sincere thank you to my parents and my sister for supporting me in everything I do.

1 INTRODUCTION

The ability to precisely control the position of a narrow beam of light has applications in a number of diverse fields. These applications include redirection of optic fiber signals from one device or fiber to another in telecommunications¹, data storage and retrieval², industrial manufacturing applications such as laser drilling or cutting³, and beam steering for radar⁴ and lidar⁵. Many of these applications require steering beams over a large (up to 40°) angular operating range at high efficiency and high operating speed.

Traditionally, in applications with large deflection angles, the desired beam steering is accomplished by individual mechanically-controlled mirrors driven by stepper motors. This mechanical solution tends to be bulky in size, and its speed and precision are limited by the mechanical movement, making them ineffective for many emerging beam-steering applications. Micro-electromechanical systems (MEMS) based devices⁶ have been developed, but they still have many fundamental practical limitations in terms of cost and size.

In contrast, a non-mechanical solution can potentially overcome the cost and size limitations of complex mechanical gimbals and steering mirror assemblies⁴. A non-mechanical beam steering solution that has received much attention involves the use of actively-controlled diffraction devices. The basic idea is to construct a diffraction grating whose diffractive pattern, and therefore outgoing beam directions, can be altered, often electronically, by changing the local optical properties of specific parts of the grating. In particular, active diffraction devices with a sub-micron grating period are desired. With such a grating period, it is possible to have a device that operates within the visible wavelength band between 400 nm and 700 nm whose non-activated grating structure would only give a 0th reflective (0R) diffractive order like an unstructured dielectric surface, and whose activated grating structure would direct part of the beam into one or more diffractive orders at high deflection angles.

For this reason, variable diffractive devices using the electro-optical properties of liquid crystals have been developed. However, the minimum required thickness of the liquid

crystal material needed to achieve the necessary birefringence limits the spatial frequency of the electrode pattern, so that these devices have a maximum deflection angle of about 10°⁴. While it is possible to achieve higher deflection angles by stacking multiple such devices⁷, this introduces multiple interfaces that decrease the overall efficiency.

Another recently demonstrated approach to electro-optical modulation uses the electrophoresis of dye ions in a solution, or an electrolyte, that permeates optically transparent nanoporous electrodes⁸. Previously, systems employing electrophoresis of pigment particles in suspension to change the optical properties of surfaces have been demonstrated⁹. However, the pigment particles in these systems agglomerate over time, resulting in limited device lifetime. This motivated the use of dye ions, which would be small enough that their mutual attraction can be overcome by thermal agitation to avoid the agglomeration problem. To compensate for the reduced absorption cross-section due to the reduction in particle size, nanoporous electrodes would be employed to increase the effective charge density of the active region.

The resulting devices, referred to here as "electrophoretic ionic optical devices", consist of a solution of dye ions contained between two nanoporous electrodes. By applying an electrical potential difference between the two electrodes, the effective optical properties of the electrodes can be modified using electrophoresis, the motion of an electrically-charged species in response to an applied electric field, to move dye ions into the pores of one of the electrodes (Figure 1.1). Given that both the ions and the voids in the nano-porous electrodes have dimensions considerably smaller than the electromagnetic wavelengths of interest (in this case, the visible wavelength band between 400 nm and 700 nm), these are not expected to cause significant scattering. Thus, the action of the relevant portion of the nanoporous electrode. Specifically, for wavelengths within one of the absorption bands of the dye, the index change would be primarily an increase in the imaginary component of the refractive index, increasing the absorption of light in the region occupied by the electrode. Thus, optical absorption by the dye ions that have been attracted into the porous electrode is responsible for the attenuation of the light in these devices.



Figure 1.1. Schematic representation of an electrophoretic ionic optical device (a) with no applied voltage, and (b) with an applied charge voltage.

Switching from pigment particles to dye ions introduced some new challenges in making electrophoretic ionic optical devices suitable for practical applications. The most difficult of these was the occurrence of irreversible electrochemical reactions that could be induced with a voltage difference between the two electrodes that exceeds a critical value of order 1 V. These reactions are undesirable as they have negative effects on the lifetime of the device. However, higher applied voltage values are desirable in order to create stronger electric fields, and thus faster ion movement and a shorter response time for these devices, and they may increase the total charge as well. To better optimize the lifetime and response time of these devices, an electron tunneling model for the onset threshold of electrochemical

reactions was developed¹⁰. Several predictions arising from the model were experimentally verified. This enabled the use of a high speed driving circuit that greatly improved the response time and lifetime of the device.



Figure 1.2. Schematic representation of a sub-micron pitch variable diffraction grating in its (a) uncharged state and (b) charged state.

One way to use electrophoretic ionic optical devices for non-mechanical beam steering applications is to construct a variable diffraction device. A variable diffraction device is made by shaping the electrodes into a series of lines, wherein specific lines can be darkened by attracting dye ions to change the period of the device, resulting in the redirection of some of the light into one or more new diffractive orders (Figure 1.2). A proof-of-principle prototype for a sub-micron pitch electrophoretic ionic variable diffraction grating was successfully implemented during the course of this study. The fabricated grating successfully modulated the intensity of a diffractive order at a deflection angle of 19° and at a sub-second switching rate. The work presented here demonstrated that sub-micron

electrophoretic ionic variable diffraction gratings have significant potential for nonmechanical beam steering application.

As this project involved ideas from a number of fields, Chapter 2 provides some background information on each of these areas.

In Chapter 3, the working principles of electrophoretical ionic optical devices are developed in more detail. Also, discussions of the selection of prototype materials and their electrical properties are included.

To overcome one of the last major outstanding issues with this type of device, a model that better predicts the electrochemical reaction onset threshold under transient condition was developed and verified as described in Chapter 4. As an application of the model, a high speed drive circuit was constructed to demonstrate the improved optimization of response time and lifetime.

In Chapter 5, the methods and the results of the measurements of the complex refractive indices of the various components making up the device are presented. The optical effects of charging unpatterned electrodes were also explored. These data were used for the modeling and the optimization of the final grating design.

Chapter 6 details the setup of the variable diffraction grating. The charging behavior of the interdigitated electrodes was observed using a large scale system. The rationale for some of the key design features is discussed. The final design parameters and modeling results are presented.

After that, the design was fabricated using direct patterning with a focused ion beam milling system. Some of the technical hurdles and solutions are discussed in Chapter 7.

Chapter 8 presents the observed performance of the fabricated device. The observed diffraction pattern agreed well with the model. The intensity modulation of a controlled diffractive order was measured. Finally, preliminary results were obtained for the response time of the grating when used with a high speed drive circuit. The results of this study

showed significant promise and suggest a number of areas for future work, summarized in Chapter 9.

2 BACKGROUND

This study incorporated ideas from a number of different fields. This chapter provides some basic principles needed to understand electrophoretic ionic optical devices and variable diffraction gratings.

2.1 Complex Index of Refraction

Since the electrophoretic ionic optical devices use optical absorption of ionic dye ions, it is helpful to review how the absorption of light is generally characterized and modeled. For the purposes of this work, the behavior of light is adequately described by the classical form of the Maxwell's equations.

Here, a simplifying assumption is made that all the media involved are linear and isotropic. The linearity is largely justified by the low electric field used in this project, and none of the material used has inherent geometrical arrangement that would lead to anisotropic behavior. Before describing electromagnetic waves through a linear, isotropic, and absorptive medium, it is useful to first consider the simpler case of a transparent medium. In this case, the external electromagnetic wave distorts the charge distribution within the medium, giving rise to induced oscillating electric dipole moments. These in turn produce electric and magnetic fields, with the net effect being a wave that travels slower than light in a vacuum. The ratio of the speed of an electromagnetic wave in vacuum, c, to the phase speed of the wave in a particular medium, v, is defined as the index of refraction, n, of that medium.

$$n \equiv \frac{c}{v} \tag{2.1}$$

The index of refraction of air at standard temperature and pressure is about 1.0003, whereas more optically dense materials differ from 1.0 considerably. For example, fused silica glass and diamond have an index of refraction of approximately 1.46 and 2.42, respectively. In general, for a given material, n depends on the wavelength of the light as

well, but this study focused on a narrow wavelength range around 650 nm within which n would vary only slightly.

According to electromagnetic theory, *n* can be determined by the relative permittivity, ε_r and the relative permeability μ_r of the medium.

$$n = \sqrt{\varepsilon_{\rm r} \mu_{\rm r}} \tag{2.2}$$

In non-magnetic materials, which includes all material considered in this study, the value of μ_r is 1, so

$$n = \sqrt{\varepsilon_{\rm r}} \tag{2.3}$$

The frequency of the electromagnetic wave does not change as it passes through different media; instead, the wavelength of the light wave changes to accommodate the change in propagation speed. This affects the amount of phase change of an electromagnetic wave as it passes through a thickness of a given material. To better explain this, consider the electric field of a plane wave propagating in the *x*-direction in a medium of index n:

$$\vec{E}(x,t) = \vec{E_0} \cos(\omega(t - \frac{nx}{c}))$$
(2.4)

where $\overrightarrow{E_0}$ is a constant vector in the *yz*-plane, ω is the angular frequency of the electromagnetic wave and *t* is time. A larger value of *n* would cause the plane wave to change phase faster spatially. The phase difference that results from local changes of *n* is important for understanding some types of diffraction grating, as discussed in Section 2.3.

In an absorptive medium, the oscillation of the internal charges can introduce energy loss. This may be thought of as "frictional" forces from interaction between atoms and molecules at close proximity. This introduces a damping term in the wave equation describing the electromagnetic wave. Mathematically, we can find solutions to this equation similar to the unattenuated plane wave solution above, except that it is needed to replace n with a complex quantity, known as the complex index of refraction, \tilde{n}^{11} .

$$\widetilde{n} = n_{\rm R} - in_{\rm I} \tag{2.5}$$

Writing the wave as the real part of a complex exponential yields

$$\vec{E}(x,t) = \operatorname{Re}(\vec{E_0}e^{(-\omega n_{\mathrm{R}}x/c)}e^{i\omega(t-n_{\mathrm{R}}x/c)})$$
(2.6)

or

$$\vec{E}(x,t) = \vec{E_0} e^{(-\omega n_{\rm R} x/c)} \cos(\omega (t - n_{\rm R} x/c))$$
(2.7)

Thus, the wave propagates in the x-direction with a speed of $c/n_{\rm R}$, as if $n_{\rm R}$ is the usual index of refraction. Furthermore, the wave amplitude exponentially decays as it propagates through the medium. In as much as the intensity of light is proportional to the square of the electric field amplitude, the rate of intensity decrease can be described by the absorption coefficient, α , of the material. The intensity, *I*, after the wave has propagated a distance *x* in the material is given by:

$$I(x) = I_0 e^{(-\alpha x)} \tag{2.8}$$

where I_0 is the initial intensity. Comparing Equation 2.7 and 2.8, it is apparent that α is related to n_1 by:

$$\alpha = 2\omega n_1 / c \tag{2.9}$$

Thus, the complex index of refraction affects the phase speed and the absorption of light as the light travels through optically different material. This was a fundamental concept in this study as it relates to the function of diffraction gratings and to optical absorption by dye ions. In particular, for ionic dye solutions with a transparent solvent, α should be directly proportional to the dye concentration, as long as the dye makes up a small part of the volume of the solution. This was important in modeling the behavior of electrophoretic ionic optical devices.

2.2 Effective Medium Theories

An effective medium theory (EMT) is used to calculate the effective dielectric constant, ε_{eff} , of a material mixture in order to describes its overall optical characteristics. The primary assumption is that the composite is made up of phases of the mixing materials with dimensions that are small compared with the wavelength of the interacting radiation, but large enough to have electromagnetic optical characteristics similar to a bulk sample of the material. In general, ε_{eff} is calculated in terms of the dielectric constants of the mixing materials, e.g ε_1 and ε_2 , and their geometrical arrangement. Several EMTs have been proposed; among the most successful ones is the Bruggeman model¹². For a mixture with two components, the model gives:

$$(1-f)\frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}} + f\frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}} = 0$$
(2.10)

where f is the volume fraction of the mixture of the component with dielectric function ε_2 .

For absorptive media, the dielectric functions are complex numbers. Nonetheless, Equation 2.3 is still expected to hold. Thus, Equation 2.10 can be rearranged to depend explicitly on the complex refractive index of the two composites, \tilde{n}_1 and \tilde{n}_2 , and the effective refractive index, \tilde{n}_{eff} .

$$(1-f)\frac{\tilde{n}_{1}^{2}-\tilde{n}_{\text{eff}}^{2}}{\tilde{n}_{1}^{2}+2\tilde{n}_{\text{eff}}^{2}}+f\frac{\tilde{n}_{2}^{2}-\tilde{n}_{\text{eff}}^{2}}{\tilde{n}_{2}^{2}+2\tilde{n}_{\text{eff}}^{2}}=0$$
(2.11)

Given the values \tilde{n}_1 and \tilde{n}_2 , it is possible to numerically solve for \tilde{n}_{eff} . This model was used in analyzing the optical properties of the nanoporous electrodes while they were submerged in ionic dye solution and when dye ions were attracted to its pores.

2.3 Diffraction Grating

A diffraction grating is a structure that has the effect of producing spatially periodic alterations in phase, amplitude or both of an incoming electromagnetic wave¹¹. In other words, an electromagnetic wave encountering such a structure would see a medium with a periodic modulation in its complex index of refraction. This introduces well-defined phase and amplitude differences between different parts of the wave exiting the structure, leading to interference that produces fringes with maxima and minima at different angular directions, which depend on the specific form of the refractive index modulation.

A simple grating to consider is an opaque sheet with multiple slits, whose width and spacing have similar orders of magnitude as the wavelength of the incoming light. A planar wavefront would see alternating opaque and transparent regions, and from the transparent openings, portions of the wavefront would emerge. Following the standard analysis for interference phenomena, it is possible to imagine that a spherical wavelet emerges from each slit. At certain outgoing angles, the spherical wavelets would line up and constructively interfere to form a bright fringe, or a diffractive order, when adjacent wavelets meet with a phase difference that are integer multiples of 2π (Figure 2.1). Since these orders are "transmitted" through the grating, the orders are named 0T, 1T, 2T, etc. based on the number of periods that is in the phase difference between adjacent wavelets, where the 0T order is the undeflected beam. For this simple transmission grating, the exit angle of the *m*th diffractive order can be determined by the grating equation:

$$a(\sin(\theta_{\rm m}) - \sin(\theta_{\rm i})) = m\lambda \tag{2.12}$$

where *a* is the period of the grating, θ_m is the exit angle of the diffractive order and θ_i is the incident angle of the light both measured with respect to the surface normal of the grating, and λ is the wavelength of the light in the region where the interference takes place.



Figure 2.1. A simple diffraction grating made from a multiple-slit assembly, showing the reconstruction of planar wavefront for the 0T, 1T, and 2T diffractive orders.

Furthermore, it is possible to have a similar effect in reflection as well, where the diffractive orders are named 0R, 1R, etc. Of course, for gratings that produce alteration in phases as well as amplitude, the grating equation has to be appropriately modified, but the naming convention remains the same. Even with these more complicated cases, the deflection angles of the diffractive order do not depend on the specific structure of the grating, but rather they depend only on the period. The variable diffraction gratings make use of this dependence on period to deflect beams into different directions in order to achieve beam steering, since as the period decreases the deflection angle of each diffractive order increases proportionally. One further note is that for gratings that have a period close to or below the wavelength of the light, it is possible to arrange the incident beam such that only the 0T and 0R order are possible, much like an unpatterned surface. By actively increasing the grating period from an initial period of this size, it is possible to cause deflected diffractive orders at large angle to appear or disappear entirely.

Lastly, while the direction of the diffractive orders are well-defined by the period of the grating, the specific intensity of each diffractive order, usually expressed as diffractive efficiency (normalized by the incident intensity), depends heavily on the specific geometry and refractive index profile of the grating. The diffractive efficiency can only be determined by solving the Maxwell's equations with appropriate boundary conditions on both sides of the grating. For this study, the diffractive efficiencies were predicted using a grating modeling software package called GSolver®, version 5.1 (Appendix A).

2.4 Total Internal Reflection

To achieve optical devices with high efficiency, the phenomenon of total internal reflection (TIR) is often used. Internal reflection refers to a reflection at an interface where the light passes from one material to another that is less optically-dense (i.e. having a smaller refractive index value) on the other side of the interface. For light approaching an interface, the direction of the refracted beam can be determined from Snell's law:

$$n_{i}\sin(\theta_{i}) = n_{t}\sin(\theta_{t})$$
(2.13)

where n_i and n_t are the refractive index value of the material before and after the interface, respectively, and θ_i and θ_t are the incident angle and transmitted angle, both measured with respect to the surface normal. Since in internal reflection n_i is larger than n_t , θ_i is larger than θ_t . Thus, it is possible to have a θ_i that results in a θ_t of 90°. This θ_i is defined as the critical angle, θ_c . When θ_i is equal to or larger than θ_c , no transmitted beam propagates past the interface and the internal reflection is total. In this case, all the incoming energy is reflected back into the incident medium. The value of θ_c can be derived from Equation 2.13 to be:

$$\sin(\theta_{\rm c}) = \frac{n_{\rm t}}{n_{\rm i}} \tag{2.14}$$

For $\theta_i > \theta_c$, Equation 2.13 can still be satisfied if θ_t becomes complex, which introduce complex components to the wave vector of the refracted wave. To see the effect of this, consider an incident wave propagating in the *xy*-plane incident upon an interface whose normal is in the *y*-direction. It can be shown¹¹ that the *y*-component of the wave vector becomes complex, and leads the following wave function for the refracted wave:

$$\overrightarrow{E_{t}}(x, y, t) = \overrightarrow{E_{t0}} e^{\mp \beta y} e^{i(k_{t}x\sin\theta_{t}/n_{ti}-\omega t)}$$
(2.15)

where k_t is the magnitude of the wave vector, n_{ti} is defined as the ratio of n_t over n_i , and β is a parameter that depends on n_i , n_t , θ_i and the wavelength of the light. Since only the negative solution is physical, Equation 2.15 describes a wave that penetrates, but does not propagate, pass the interface and then decays exponentially away from the interface. This is known as the evanescent wave. The depth of penetration can be characterized by β . Typically, the amplitude of the evanescent wave becomes negligible within a distance of a few wavelengths from the interface.

Note that energy conservation is not violated, as it can be shown that the energy circulates back and forth across the interface, so that there is no net flow of energy through the interface. However, the TIR can be "frustrated" if a medium with an appropriate index of refraction is placed in the region within which the evanescent wave penetrates, which is sometimes referred to as the evanescent zone (Figure 2.2a). Given a medium with a sufficiently large refractive index value, Snell's law no longer requires θ_t to be complex and thus the wave can behave again as a travelling wave and propagate into this new medium (Figure 2.2b). Alternatively, if an absorptive medium whose complex index of refraction has a strong imaginary component at the wavelength of the light is placed within the evanescent zone, energy within the evanescent wave would be absorbed by this medium (Figure 2.2c). In both cases, to satisfy the conservation of energy criterion, the reflected beam can no longer have the equivalent energy intensity of the incident beam. Therefore, it is possible to control the intensity of the reflected beam by modifying either the real and/or imaginary component of the complex refractive index within the evanescent zone.

In the context of this study, the reflective diffraction gratings were tested in an appropriate configuration that used TIR to ensure that no light propagated deep past the nanoporous electrode into the bulk dye solution, where it would be absorbed and lost. At the same time, to increase absorption within the nanoporous electrodes, we selected refractive index combinations for which the light would travel through the absorptive electrodes before TIR occurred at the electrode-solution interface. As such, even though some of the absorption of the reflected beam was due to the frustration of TIR from the dye ions in the bulk solution, where the dye concentration was not directly controlled, a large part of the optical absorption of the reflected beam occurred within the electrode region where the dye concentration was actively controlled.



Figure 2.2. Frustrated total internal reflection: (a) With no medium in the evanescent zone, TIR occurs and all the energy goes into the reflected beam. (b) With the introduction of a high index medium in the evanescent zone, TIR is frustrated because some of the energy propagates past the second interface. (c) TIR is frustrated by introducing an absorptive medium in evanescent zone.

2.5 Electric Double Layer

Since this study involved applying charge to electrodes in ionic solution, it is useful to briefly review how the ions arrange themselves in the vicinity of a surface charge imbalance on an electrode. It is well-known that a charged conductor has all its charge imbalance on its surface. Due to electrostatic attraction, ions within an adjacent solution develop an opposite net charge imbalance in a layer near the electrode surface. Together, these two layers of charge imbalance are known as the electric double layer. However, the ions are much larger, more massive and much less numerous than electrons, which causes the spatial distribution of the ionic charge imbalance to be very different than that of the electrons.

One of the most widely accepted models of the electric double layer is the Guoy-Chapman-Stern (GCS) model, which describes the charge distribution near the electrode as consisting of a compact layer and a diffuse layer of ions¹³. For simplicity, consider that there is only one kind of ion present, each have a single charge which is opposite in polarity to the sign of the charge imbalance at the electrode surface. Within the region closest to the electrode, the electrostatic forces are sufficiently strong to uniformly pack the ions with a density approaching a certain maximum concentration to form the compact layer. These ions shield the surface charge to some degree, therefore reducing the magnitude of the local electric field outside of the compact layer to the point where the electrostatic forces no longer dominate over the thermodynamic behavior. As a result, thermal agitation becomes significant for ions outside of the compact layer in the region known as the diffuse layer. Of course in reality there is a continuous transition throughout, but the important aspect is that there is a long "tail" to the distribution in which the concentration of ionic species approaches the value "at infinity", so this simple model is helpful computationally.

The thickness of the compact layer is generally several angstroms (Å), beyond which the ions become susceptible to thermal agitation. While the distribution of ions is continuous, for the purpose of modeling, the ions in the diffuse layer can be considered as arranged in discrete thin sheets, or laminae, parallel to the electrode, which are in thermal equilibrium with each other. Since the electrostatic potential varies with distance from the surface, the ions in each lamina have a corresponding energy which at equilibrium implies that concentrations of the ions are related by a Boltzmann factor. Defining a reference lamina far from the electrode, where the equilibrium concentration of the ion species has a bulk concentration value of n^0 , the concentration, n, in any other lamina is thus described as

$$n = n^0 \exp(\frac{-ze\phi}{kT}) \tag{2.16}$$

where ϕ is the electrostatic potential of the lamina measured with respect to that of the bulk solution, *e* is the charge of an electron, *z* is the signed charge magnitude on the ion in units of *e*, *k* is the Boltzmann constant, and *T* is the absolute temperature.

Using the Poisson equation from electrostatics, it is possible to show that the potential within the diffuse layer drops off exponentially with a characteristic length of $1/\kappa$, where

$$\kappa = \left(\frac{2n^0 z^2 e^2}{\varepsilon_{\rm r} \varepsilon_0 kT}\right)^{1/2} \tag{2.17}$$

is known as the Debye-Huckel parameter. Here, ε_r is the relative permittivity of the environment just outside the electrode, which may not be the same as that of the bulk solvent, and ε_0 is the permittivity of free space. Thus, the double layer becomes thinner at higher bulk concentration. For example, for an electrolyte with one type of cation and one type of anion both with a charge magnitude of 1 in 25 °C water, a 1 M solution would have a diffuse layer with a characteristic length of 3.0 Å, while a 1×10^{-4} M solution would have a characteristic length of 304 Å.

Given the small separation between the two layers of charge, electric double layers behave as capacitors with counter-intuitively large capacitance per unit area. This fact has been widely used in the development of supercapacitors. As a first order approximation, it is possible to model the electric double layer as a parallel plate capacitor, using the characteristic length as the separation. The capacitance of a parallel plate capacitor is given by:

$$C = \frac{\varepsilon_{\rm r} \varepsilon_0 A}{d} \tag{2.18}$$

where A is the surface area of the plate and d is the separation between the plates. For example, for a solution of 1 M in 25 °C water, and an area of 1 m^2 , the capacitance would be above 2 F. This area is readily achievable especially with the use of porous electrodes. The double layer, therefore, provides a way to reversibly store a large amount of charge on a surface with only a modest amount of voltage. This characteristic was also exploited, for a different reason, in this study as well.



Figure 2.3. Simple electrical models of an electrochemical cell (a) with no electrochemical reactions (b) with electrochemical reactions.

In a simple electrochemical cell (hereafter referred to as a cell) with two electrodes comprised of the same material that is submerged in an electrolyte, each electrode has its own electrical double layer. In terms of circuit analysis, since ideally no electrochemical reaction is taking place, such a cell can be modeled as two separate capacitors with a resistance, R_{bulk} , in the middle, which represents the frictional resistance to ion movement within the bulk solution between the two electrodes. Since it is impossible to measure the

charge on just one of the two electrodes, their capacitances is often considered to be combined as the overall cell capacitance, C (Figure 2.3a). The size of this capacitance can be determined with a simple test circuit employing an external series resistor, with resistance $R_{\rm s}$. By measuring the voltage across this series resistor, $V_{\rm R}$, we can calculate the current, I, over time after applying an input voltage step with amplitude $V_{\rm in}$ (Figure 2.4).

$$I(t) = \frac{V_{\rm R}(t)}{R_{\rm s}} \tag{2.19}$$



Figure 2.4. Circuit used to measure the overall cell capacitance of an electrochemical cell.

Then, the total charge built up in each of the double layer can be determined by integrating the current up to the point when the current of the system vanishes in the fully charged state. In this state, the only voltage drop in the circuit is through the cell capacitance, so we can use $V_{\rm in}$ to find its value.

$$C = \frac{\int_{t=0}^{\infty} I(t)dt}{V_{\rm in}}$$
(2.20)

It is well known that when too large a voltage (typically about 1 V) is applied across the two electrodes of a cell, electrochemical reactions can be induced, at least after the transient charging phase. The reaction allows some charge to pass though the double layer, giving rise to a "faradaic current". Therefore, the electrical model has to be modified by adding a resistance, R_{faradaic} , parallel to the cell capacitance (Figure 2.3b). In this case, the current remains non-zero even after the electric double layers have been fully charged. The onset of such electrochemical reactions is known to be surprisingly sharp with increasing cell voltage. Thus, tracking any sudden increase in this steady state current provides a way to monitor the presence of electrochemical activity in the cell.

It should be noted that a similar electric double layer also exists around individual charge particles in an electrolyte. Effectively, by electrostatic forces, each charged particle influences the spatial distribution of the other charged particles around itself. The length scale of this interaction can also be characterized by $1/\kappa$. This effectively increases the size of ions when considering their movement through a fluid, such as during electrophoresis.

2.6 Electrophoresis

Electrophoresis is the induced movement of charge particles in an electrolyte by an external electric field. Each particle is acted upon by two opposing forces: the electrostatic force and the Stoke's shear force, which is a velocity-dependent frictional force. The particle thus reaches a terminal velocity for which the two forces are equal. Under moderate applied field strength, the terminal speed of the particle, v, is directly proportional to the local electric field, E. Thus the two can be related by a proportionality factor known as the electrophoretic mobility, μ .

$$v = \mu E \tag{2.21}$$

The electrophoretic mobility itself depends on a number of parameters, and the specific relationship tends to be quite complicated. Here, a simplified model is presented to gain insight into some of the key parameters on which μ depends and to obtain approximate

results¹⁴. The basis of the model equates the electrostatic force and the shear force acting on the particle, where it is assumed that the particles are rigid spheres. Also, it is assumed that the particle size is small compared to the characteristic length of the electric double layer around the particle, $1/\kappa$, as defined in Equation 2.17, which is valid for the ions used in this study. With a relatively thick diffuse layer, it can then be assumed that the amount of opposite charge within the compact layer, which is expected to travel with the particle, to be small compared to the overall charge of the particle, q. Thus, the electrostatic force acting on the ensemble is

$$F_{\rm e} = qE \tag{2.22}$$

For a small sphere moving a moderate speed within a viscous fluid, the shear force, F_s , is given by Stokes' equation:

$$F_{\rm s} = 6\pi\eta r_{\rm eff} v \tag{2.23}$$

where η is the viscosity of the fluid and $r_{\rm eff}$ is the effective hydrodynamic radius of the charge particle. $r_{\rm eff}$ is larger than the actual size of the particle itself because of the electric double layer formed around it. Nonetheless, this can be approximately determined by measuring the diffusion constant, D, of the particle within the fluid:

$$D = \frac{kT}{6\pi\eta r_{\rm eff}} \tag{2.24}$$

Equating Equations 2.22 and 2.23 to obtain an expression for μ :

$$\mu = \frac{v}{E} = \frac{q}{6\pi\eta r_{\rm eff}} \tag{2.25}$$

It should be noted that μ is inversely proportional to the size of the particle. Using Equation 2.25 and knowing the diffusion constant, it is possible to derive an approximate value for μ , bearing in mind the simplifying assumptions made.

3 ELECTROPHORETIC IONIC OPTICAL DEVICES

Here, we use the term electrophoretic ionic optical devices to mean devices in which ions are moved by electrophoresis to modify the local optical properties of a specific region. Although this idea is applicable to a wide choice of ions and electrodes, this study focused on a setup to attract methylene blue dye ions into transparent zinc antimonate nanoporous electrodes to controllably increase its absorption. This section provides detail of how electrophoretic ionic optical devices function, as well as the rationale for the specific choice of dye solution and electrode material.

3.1 Working Principle of Electrophoretic Ionic Optical Devices

The basic idea of these devices is to controllably cause a region in and around a transparent nanoporous electrode to exhibit higher optical absorption by electronically attracting dye ions to the electrode. In order to attract enough dye ions, the device uses the high capacitance of the electric double layer to store a significant amount of charge with a relatively low voltage. Even so, since individual ions have a small absorption cross-section, nanoporous electrodes are needed to further increase the surface area within the electrode volume and the total attracted charge. The pores should be tens of nanometers in size, which are much smaller than the wavelength range for visible light and therefore do not cause incident light to scatter significantly. It is important to note that it is not necessary that the porous layer have a high lateral conductivity since the substrate could first be coated by a thin, non-porous, transparent conductive layer to provide the lateral conductivity.

This principle method of modulating optical properties electrically offers a number of unique advantages. First, since the ions are small enough (approximately 1nm in diameter) to be significantly affected by thermal agitation, the system can be expected to be in thermodynamic equilibrium at most times and should therefore exhibits little hysteresis. Also, the dye ions are not expected to come out of solution and should therefore remain mobile within the solution indefinitely. Secondly, this type of device does not experience crosstalk issues that occur in liquid crystal-based devices; it can be expected to function even with small electrode feature size, provided that such small features can be fabricated.

Thirdly, this principle allows sufficient freedom with regards to the shape and geometric arrangement of the electrodes, so that these devices can be adapted to a wide number of applications.



Figure 3.1. Schematic representation of the ion distribution and the spatial profile of the electrolyte electrical potential of an electrophoretic ionic optical device (a) with no applied voltage, (b) immediately after the application of an applied charged voltage, and (c) after the system has reached steady state.

Typically, an electrophoretic ionic optical device would involve two nanoporous electrodes submerged in an ionic dye solution with only one type of cation and one type of anion. Figure 3.1 shows a simple setup where a solution with dye cations and transparent anions has been sandwiched between the two nanoporous conductive thin films. Before voltage is applied, the dye is expected to distribute itself uniformly throughout the solution. Immediately after a voltage difference is applied, assuming a planar geometry, a roughly
uniform electric field would be set up between the two electrodes, and both types of ions would move towards the electrode with the opposite charge by electrophoresis. Therefore, the magnitude of the electric field and thus the speed of the ion movement would be directly proportional to the magnitude of the applied voltage. The movement of both types of ions would contribute to the overall measured current. In this transient state, as both types of ions collect in the electric double layers around the two electrodes, the electric field immediately outside the electrodes would increase dramatically, while the growing layer of accumulated ions would shield the electric fields from the bulk solution. A steady state is reached when no electric field penetrates into the bulk solution, so that there is no potential gradient far away from both electrodes. The charging results in creating a high concentration of dye ions within and around the pores of one of the electrodes. For wavelength within the absorption band of the dye, the increased concentration of dye ions in one of the porous electrode would significantly increase the complex component of the effective refractive index within that electrode. Thus, light would be significantly attenuated as it propagates through this region compared to the uncharged case. To achieve high efficiency and contrast, TIR can be used to prevent light from transmitting into the bulk dye solution, where the absorption is not controlled.

It is notable that this setup resembles an electrochemical cell used to drive an electrochemical reaction. For the function of this device, however, any irreversible electrochemical reaction is highly undesirable as it adversely affects the lifetime of the device. This was a major hurdle to overcome in order to make practical devices, and it will be dealt with in Chapter 4.

3.2 Selection of Material for Prototype

The prototypes used in this study were made with zinc antimonate nanoporous electrodes submerged within a methanol solution with methylene blue (MB) dye. Previous studies have shown that the desired variable absorption effect can occur in various transparent porous conductors having a large relative effective surface area, including carbon nano-tube films and porous indium tin oxide (ITO) films formed by glancing angle vacuum deposition. Similarly, numerous ionic dyes in numerous electrolytes may be employed^{8, 9}. Here we

focused on what are felt would be the most reliably reproducible electrode and dye combination. This section outlines the rationale of choosing this combination for the purpose of prototyping.

3.2.1 Methylene Blue Ionic Dye in Methanol Solution

Having chosen to work with absorption, the electrolyte of the device must be an ionic dye solution that has at least one absorption band within the visible spectrum (about 400 to 700 nm). Moreover, it was desirable, at least initially, to have the absorption band towards the longer wavelength, or red, end of the visible spectrum, in order to use a longer wavelength light to obtain a larger deflection angle with a grating of a given period, which is limited by the fabrication method. Based on these requirements, MB dye was chosen for use for prototyping during the course of this study (Figure 3.2).



Figure 3.2. Molecular structure of MB dye.

MB is a dye used often in biological and chemical experiments. It has a broad absorption peak around 655 nm, in the red part of the visible spectrum as required (Figure 3.3). However, this peak has been shown to shift with the pH of the solution ¹⁵. Since electrophoresis can also change the pH of an aqueous solution around the electrodes, it was decided that HPLC grade methanol would be used as the solvent to avoid the unnecessary complexity.



Figure 3.3. Absorption properties of MB dye dissolved in methanol.



Figure 3.4 Setup used to measure dissociation rate of an ionic dye solution.

To be an effective electrolyte of electrophoretic ionic optical device, it was verified that most of the MB dye in solution indeed dissociated into ions. Using an experimentally measured diffusion constant¹⁶ and the approximate model presented in Section 2.6, the amount of dissociation of MB dye in methanol was verified to be reasonably close to 100%. This was done by measuring the ionic current through solution within a long glass tube with a high direct current (DC) voltage applied across two copper wire electrodes on each end of

the tube (Figure 3.4). The tube was sufficiently large so that the shear force on the fluid movement by the tube wall would not significantly affect the flow of the ions. Different voltages between 5 to 50 V were applied, sufficiently high to ensure that the resulting electrochemical reaction took place at a high rate such that the equivalent faradaic resistance would be negligible. This ensured that there was only a negligible amount of charge held in the electric double layer to prevent significant capacitive voltage drop from being introduced. Therefore, the measured current, I, would give the rate of ion movement limited almost entirely by the fluidic resistance. Thus, this current can be related to the drift speed of individual ions, v, and the number concentration, n, of the ions by the following equation:

$$I = nvAq \tag{3.1}$$

where A is the cross-sectional area of the glass tube and q is the charge on each ion, which for MB dye is equal to the charge magnitude of one electron. The value of v was calculated by using the electrophoretic mobility and the electric field strength approximated by assuming uniform electric field within the glass tube. Finally, comparing the calculated value of n and the amount of dissolved dye in the solution gave a measure of how much dissolved dye molecules dissociate into cation-anion pairs. For different MB in methanol solutions with molar concentration ranging from 1.73 mM to 1.73 μ M, the rates of dissociation were all measured to be larger than 84%. A number of approximations were made in deriving the result, but it can be concluded that the dye was largely dissociated in methanol and could be moved by electrophoresis.

The MB-methanol solution was shown to have the appropriate optical absorption band and a sufficient dissociation rate. For these reasons, it was chosen as the electrolyte for the prototypes made throughout this study.

3.2.2 Zinc Antimonate Transparent Nanoporous Conductive Thin Film

To construct electrophoretic ionic optical devices with the largest change in absorption properties, the nanoporous electrodes should be made of a transparent conductor, and should

be sufficiently porous. Also, ease and repeatability of fabrication were desired. Zinc antimonate $(ZnSb_2O_6)$ conductive thin film satisfied all of these requirements.



Figure 3.5. A scanning electron microscope image of a cleaved face of a typical nanoporous ZnSb₂O₆ film.

 $ZnSb_2O_6$ is a transparent conductor that is available in the form of 15 nm nanoparticles in dispersion¹⁷. This dispersion was made into a nanoporous thin film by a common spin coating technique. The films were applied onto a nominally 25 mm × 25 mm square float glass substrate having a nominally 20 nm thick ITO coating¹⁸, which provided the lateral conductivity while maintaining transparency. The thickness of the $ZnSb_2O_6$ coating was controlled by changing the spin speed of the spin coater and more significantly by adjusting the viscosity of the dispersion by suspending additional polyethylene glycol (PEG) in the dispersion. Once coated, the samples were heated to 450 °C to evaporate out the liquid component of the dispersion and the PEG, leaving a nanoporous coating (Figure

3.5). While it is true that the square substrate created some non-uniformity in film thickness at the corners, those parts were mainly use for attaching electrical connections and were not exposed to the electrolyte during testing. The detail procedure of preparing a nanoporous $ZnSb_2O_6$ sample can be found in Appendix B.

The availability of this spin coating technique allowed the fabrication of transparent nanoporous electrodes with high repeatability in thickness. To quantify this, five samples were prepared using a suspension with a ratio of 1 part PEG to 64 parts $ZnSb_2O_6$ dispersion and spun at 3000 rpm. The thickness of each sample was measured by removing a region in the resulting thin film with the tip of a pair of wafer tweezers and measuring the depth of the resulting void with an Alpha Step 200 profilometer. Each sample was measured in four different locations. Overall, the thin film was measured to have a mean thickness of 656 nm +/- 5 nm. Subsequent scanning electron microscope (SEM) scan revealed that the true thickness of these films should be around 800 nm, suggesting that the profilometer might have slightly modified the nanoporous film during measurement. Nonetheless, the profilometer thickness data was still valid as a relative measurement. Thus, the spin coating technique was demonstrated to deliver the desired repeatability in thickness.

The porosity of $ZnSb_2O_6$ was indirectly measured by comparing the double layer capacitance around a $ZnSb_2O_6$ nanoporous electrode with that of a flat ITO electrode with the same lateral area exposed to the electrolyte. Increase in capacitance, to first order, would be directly proportional to the increase of available surface area due to the presence of the pores, which in turn would be roughly directly proportional to the thickness of the film. Using the procedure outlined in Section 2.5, the double layer capacitance of the film was measured in refillable test samples, hereafter referred to as "test cells".

These test cells were comprised of two electrodes in the form of conductive thin films deposited on separate 25 mm \times 25 mm \times 1 mm ITO coated float glass slides substrates. A sealed compartment was formed by clamping these samples onto the top and bottom of an acrylic o-ring holder, which was fitted with two fluid ports to allow for filling and draining of the compartment using a syringe (Figure 3.6). The area of each electrode exposed to the

solution was a circle with a diameter of 12.6 mm. Electrical connections to the electrodes were made using 32 AWG copper wires attached by electrically-conductive silver epoxy¹⁹.



Figure 3.6. (a) A sectioned side view and (b) a sectioned top view of the test cell structure.

With this setup, the capacitance of each film was observed to increase roughly in a linear fashion with thickness, consistent with expectations (Table 3.1). For a layer 800 nm

thick, the increase in effective area was over 36 times compared to a flat ITO film of the same area exposed to the electrolyte.

Film Thickness	Capacitance	Capacitance- Thickness Ratio	Effective Area Increase Factor
(nm)	(µF)	(µF/nm)	
6890	4351	0.631	306
1130	734	0.649	52
800	542	0.677	38

Table 3.1.	Measured capacitance of electrochemical cells with two ZnSb ₂ O ₆
	nanoporous electrodes of various thicknesses.



Figure 3.7. A logarithmic plot of a typical charging current of an electrochemical cell with nanoporous electrodes over time. The curvature in the plot indicates that the relationship is not a simple exponential decay.

During this measurement, however, it was observed that the cell charging behavior deviated from a simple linear resistor-capacitor combination, in which the current would decay exponentially as a function of time. With the nanoporous electrode, a curvature was observed in the plot of the logarithm of the current vs. time, thus indicating that the current did not exhibit a simple exponential decay (Figure 3.7). The bulk resistance of the cell, related to the bulk ion concentration, was not expected to change significantly during charging and discharging, since the amount of charge moved was small compared to the total

amount of dye ions in the solution. Therefore, it was suspected that the cell capacitance increased over time to give this curvature. This could be attributed to the relatively longer time required for an ion to come into contact with the electrode area deeper within the pores, so that the available area slowly increased over time as the ions reached deeper into the nanoporous electrode. Thus, the capacitance increased over time and reduced the time constant of the charge curve. While noteworthy, it was reasonable to expect this to be true for all nanoporous electrodes, so this did not affect the choice of electrode material.

It was also necessary to verify that the electrode material was able to withstand a moderate amount of applied voltage difference without causing electrochemical reaction. To determine the electrochemical threshold voltage, a staircase voltammetry technique¹³ was applied, wherein increasing steps of DC voltage from a DC power supply was applied across a test cell with two 800 nm thick ZnSb₂O₆ films and a series resistor for measuring the current. At each DC voltage setting, the system was allowed to reach steady state over 30 s so that the steady state current could be measured (Figure 3.8). This test was done with MBmethanol solution at three different concentrations. Results with electrolyte of different concentrations had similar steady state current up to about 1.2 V. It was not well understood why the steady state current even at low voltage was non-zero, though it was consistent across different concentrations. Since the bulk solution resistance decreases dramatically with increasing ion concentration, it was likely that this current did not arise from dye ions traveling through the bulk solution and therefore not through the electric double layers either. Beyond 1.2 V, the steady state current increased dramatically, with the highest concentration showing the greatest increase of current level with increasing voltage. This was more consistent with the expected behavior of electrochemical reactions involving the dye ions. Therefore, the electrochemical voltage threshold was determined as 1.2 V, which was typical of such systems.

Given the favorable optical properties, repeatable fabrication, nanoporous characteristics, and electrochemical characteristics of $ZnSb_2O_6$, it was chosen as the prototype electrode material for this study.



Figure 3.8. Steady state current with increasing applied voltage for a cell composed of nanoporous ZnSb₂O₆ electrodes with different MB dye concentration.

4 ELECTROCHEMICAL LIMIT

It was noted that several practical hurdles would have to be overcome in employing electrophoretic ionic optical devices in practical applications, such as developing practical means for permanently encapsulating the required electrolyte, and ensuring long operation life under a variety of circumstances. In all these cases there are reasonable prospects for such developments and for this reason here considerable attention was placed on the fundamental electrochemical issues that lie at the core of this application problem.

In general, the speed at which the ions move in response to the applied field increases with the magnitude of the field. Achieving a substantial change of optical properties in electrophoretic ionic optical devices at video rates has been found to require a voltage of at least several volts applied across the electrode, which is incompatible with our observation that sustained application of more than roughly 1 V between the electrodes leads to irreversible electrochemical reactions, which can result in deterioration of the electrode material. These reactions are undesirable since they limit the long-term performance of the device.

Therefore, in order to increase the response rate of such devices while maintaining a long operating life, it was helpful to develop an improved understanding of the physical mechanisms underlying the onset of these electrochemical reactions. Much research has taken place regarding the onset of electrochemical reactions²⁰, but to the author's knowledge there had been no exploration of this mechanism in largely transient situations, where a device is modulated at a relatively high (for example, greater than 10 Hz) frequency and consequently the current associated with the charging double-layer capacitor is much greater than any electrochemical reaction current.

Electrochemical reactions have previously been described as a quantum tunneling phenomenon in which an electron moves between an electrode and an ion across a non-specific energy barrier^{13, 21, 22}. Here¹⁰, this idea was further developed to describe the onset of electrochemical reactions in terms of the local electric potential energy gradient (i.e. the electric field) at the nanometer length scale near the electrode surface. This description led

to the hypothesis that it is the magnitude of the local (i.e. nanoscale) surface charge density on the electrode, rather than the magnitude of the applied voltage producing that surface charge, that determines the local rate of electrochemical activity. Further, consistent with previous treatments, this approach predicted a simple dependence of the threshold applied voltage on the bulk concentration of the solution. Moreover, this tunneling model led to the new prediction that for a given applied voltage, the electrochemical activity would be enhanced near convex surface features that are small compared to the double layer thickness, since the local electric field and hence the rate of tunneling near these regions would be higher. For reactions that cause removal of material, this would result in surface smoothing on the nanometer size scale. The experiments described here confirmed these predictions. When applied to electrophoretic ionic optical devices, this new understanding suggested an optimal voltage vs. time profile for reducing the transition time between optical states without inducing electrochemical reactions.

4.1 Electron Tunneling Model of Electrochemical Reactions

Since the electrochemical reactions discussed here arise from electron quantum tunneling, it is helpful to consider the key principles of this phenomenon. In a typical electron tunneling situation, with a potential energy barrier of finite height and width, there are two requirements for achieving a significant tunneling rate (Figure 4.1). First, the total energy of an electron on one side of the barrier must exceed the potential energy on the other side. Second, the barrier height and thickness must be sufficiently small, because the tunneling probability generally diminishes quickly with respect to these parameters. For example, in the case of a square potential barrier, the tunneling probability decays exponentially with the product of the thickness and the square root of the height the energy barrier²³. In quantum tunneling experiments, significant tunneling is typically observed when the thickness of an energy barrier is reduced to atomic dimensions. Here, the range of conditions for which both of these requirements may be met in the case of ions in solution near an electrode is explored.



Figure 4.1. Schematic of the requirements for significant electron tunneling through a potential energy barrier, the probability of tunneling is represented by the square of the amplitude of the oscillation of the probability amplitude function (ψ): (a) no tunneling occurs because the potential energy (V) past the potential barrier is greater than the total energy of the electron (E); (b) even though the energy requirement is met, only a small amount of tunneling occurs because the width of the barrier is too large; (c) significant tunneling occurs because both requirements are met. We are interested in non-spontaneous electrochemical reactions; that is, reactions that do not occur at an appreciable rate in the absence of a voltage externally applied to the electrodes. There are two types of reactions of interest – reduction and oxidation. The reduction reaction considered here involves a positive ion (cation) gaining an electron from a negatively charged electrode. This electrode, where reduction occurs, is called the cathode. Similarly, the oxidation reaction involves a negative ion (anion) losing an electron to a positively charged electrode, called the anode in the case of oxidation. In both cases, if the applied voltage is sufficiently high, an electron would transfer between the ion and the electrode. As mentioned earlier, in the area of interest to this particular work, such electrochemical reactions are undesirable and the aim was to avoid conditions for which they occur.

The basic physics is very similar for the two reaction types. Let us first consider the case of a positive ion receiving an electron from a negative electrode. In order for this reduction reaction to not occur spontaneously at zero applied voltage, the energy of the highest occupied electron state in the electrode (hereafter referred to as the electrode state) should be lower than that of the lowest unoccupied state in the ion (the ion state), as shown in Figure 4.2a.

Consider first the electrode state. Its energy is related to the work function of the material and, within the range of voltages considered in this study, is constant regardless of the voltage and charge applied to the electrode, since the voltage is sufficiently small that the electron configuration inside the conductor remains unaffected. Now consider the ion state. For a positively charged ion, an electron moving to it would do so under the influence of an attractive electric force, and thus it would be moving to a point of lower potential energy relative to the region surrounding the ion, so the ion can be represented by a potential well.

The situation becomes more interesting when a voltage is applied between the two electrodes, because the resultant electric field creates a spatial distribution of electrical potential in the solution. This means that the energy of the ion state will depend on the position of the ion, because the ion state energy would be equal to the ambient electrical potential at a given point minus the depth of the ion potential well. This situation is depicted in Figure 4.2b and c.



Figure 4.2. Schematic of the evolution of the relative potential energy difference (ΔV) between the negative electrode (anode) and cations during the reduction of the ion with (a) no accumulated charge, (b) insufficient charge such that the only ions with states of low enough potential energy is too far to give significant tunneling probability and (c) sufficient charge to allow tunneling and reduction to occur. (d) to (f) describe similar steps for the oxidation of an anion.

We can now consider the implications of this arrangement on the quantum tunneling rate that enables an electrochemical reaction to occur. As mentioned earlier, there are two requirements for such tunneling to occur – the ion should be sufficiently close to the electrode to allow the tunneling probability to be non-negligible, and it should be sufficiently far from the electrode to enable the applied electric field to bring the energy of the ion state down below that of the electrode state. The distance required to do this would decrease as the applied electric field is increased. Thus, at a low electric field level as illustrated in

Figure 4.2b, the position at which the reaction becomes energetically favorable is located too far from the electrode to enable a significant tunneling rate, whereas in Figure 4.2c, illustrating a higher electric field, that distance is reduced to a point where the tunneling probability is non-negligible. While the general idea of reaction states and tunneling are well known in the electrochemical literature, to our knowledge this is the first description that clearly identifies the rate-determining phenomena to be a combination of both the probability that an electron would tunnel across a spatially defined energy barrier, and the favorability from an energy perspective that depends on the ion state energy and the ion position in an applied electric potential energy gradient.

As mentioned previously, the physics is very similar in the complementary case of a negative ion releasing an electron to a positive electrode. Even though the electron is leaving a net neutral atom, the negative ion has an electronic configuration such that energy is required for the electron to escape to the surrounding region and thus the electron lies within a potential energy well relative to the ambient potential that would be present at that position if the ion were not present. Figure 4.2d, e, and f show, respectively, the corresponding cases of the reaction being energetically unfavorable with low electric field strength, being energetically favorable but of very low tunneling probability at with an intermediate electric field strength, and being favorable from both perspectives, for ions in a limited range of locations, at a higher electric field strength.

From this perspective, let us now consider the spatial distribution of the electrical potential in the electrolyte in a bit more detail. Generally, the distribution of electrical potential is determined from simple electrostatic considerations, because the current associated with electrochemical reactions at and just beyond the threshold conditions for electrochemical reaction is negligible. The electrical potential difference, $\Delta \phi$, between a position just outside the electrode and a specified point located at a distance, x, from the surface of the electrode, is simply the integral of the electric field along the path. If the geometry is planar and x is measured in the normal direction from the electrode surface, this relationship is described by Equation 4.1.

$$\Delta\phi(x) = -\int_{0}^{x} E(x') \cdot dx'$$
(4.1)



Figure 4.3. Gaussian surface used to determine the magnitude of the electric field at different distances from the electrode. *dA* is taken to be much smaller than the overall exposed electrode surface area.

In turn, the spatial distribution of the electric field can be determined by Gauss' law using a Gaussian surface in the shape of a box, as shown in Figure 4.3. For distances sufficiently close to the electrode, the enclosed charges in the electrolyte are very small compared to the surface charge density on the electrode, σ_e , and so to a good approximation the magnitude of the electric field is defined by σ_e , as shown in Equation 4.2, where ε_{eff} is the effective permittivity of the electrolyte in the surface region, which may be somewhat lower than the value in the bulk.

$$E(x \cong 0) = \frac{\sigma_{\rm e}}{\varepsilon_{\rm eff}} \tag{4.2}$$

At greater distances, this approximation fails since the opposite charges attracted within the electrolyte become more significant, gradually reducing the field to near zero at distance significantly greater than the Debye length²⁰. Although the field profile is less simple in this case, the same basic tradeoff between energetic favorability and quantum tunneling likelihood applies – only at sufficiently long distances is the reaction energetically favorable and only at sufficiently short distances is the quantum tunneling probability non-negligible, and only if the electrode surface charge density is sufficiently high is there a significant overlap of these two regions in which an appreciable electrochemical reaction rate can take place.

This quantum tunneling description provides a clearer explanation of the onset of electrochemical reaction based on the local electric field in the vicinity of the electrode surface than does the common description based on the applied voltage in the well-studied planar electrode/steady-state case, where the potential of the electrode with respect to the bulk solution is simply proportional to the charge. For transient and/or non-planar cases, this is no longer the case, and the quantum tunneling description led to three predictions, described below, which have been experimentally verified in order to help validate this model.

4.2 **Predictions Arising from the Electron Tunneling Model**

The electron tunneling model gave rise to three predictions. First, the onset of electrochemical reaction should be directly related to the accumulated surface charge density on the electrodes, instead of the applied cell voltage. Second, changing the bulk concentration of the solution should introduce an offset in the electrochemical reaction threshold cell voltage. Finally, near the electrochemical reaction threshold charge, smoothing of nanometer-sized bumps should occur at the electrode surface for electrochemical reactions that cause removal of electrode material. These three predictions are described in more detail below.

4.2.1 Accumulated Charge as Onset Indicator of Electrochemical Reactions

A key prediction of the quantum tunneling model was that the onset of electrochemical reaction would be directly linked to the local electric field density near the electrode surface. This local electric field is directly proportional to the local surface charge density on the electrode which is the time integral of the current per unit area associated with charging the double-layer capacitor. At steady state, this charge density is proportional to the applied voltage, but this is not the case under transient conditions in which the charging current results in additional voltage drop in the electrolyte and/or the electrodes. Thus, the local surface charge density on the electrode, rather than the applied voltage, would be the most direct predictor of the degree to which electrochemistry will occur.

This link between the electrochemical activity level and the local charge density on the electrode has an important implication for electrophoretic ionic optical devices, because it means that the transition time between two optical states can be reduced by applying a sufficiently high voltage without inducing an electrochemical reaction, provided the total accumulated surface charge density on the electrode have been maintained below a predetermined threshold.

4.2.2 Effect of Bulk Concentration on the Threshold Applied Voltage

By considering the spatial distribution of potential energy between the electrodes, the model predicted that for a given applied surface charge density, the applied voltage that produces it would depend on the bulk concentration of the solution in a location comparatively far away from the electrode. To understand this, it is important to consider the distribution of electrical potential in the solution at different locations between the two electrodes. Since an electric double layer exists around each electrode, the total potential, ϕ_{tot} , is defined as the difference in electrical potential at a location inside the electrode and at a location in the solution far from the electrode. Following the GCS model presented in Section 2.5, the charge distribution near the electrode can be described as consisting of a compact layer and a diffuse layer of ions. As shown in Equation 4.3, from the perspective of the CGS

approximation, this voltage can be broken down into three parts, the potential difference across the electrode-solution interface, $\phi_{\rm e}$, the potential difference across the compact layer, $\phi_{\rm c}$ and the potential difference across the diffuse layer, $\phi_{\rm d}$ (Figure 4.4).



$$\phi_{\rm tot} = \phi_{\rm e} + \phi_{\rm c} + \phi_{\rm d} \tag{4.3}$$

Figure 4.4. Schematic of (a) the potential profile and (b) the ion concentration profile from inside the electrode through the electric double and into the bulk solution; the dotted line represent the profiles for a system with larger bulk concentration. For a given applied surface charge density, the first two terms should be relatively constant for different bulk concentrations, but for different reasons. The first term, ϕ_e , is related to the work function of the electrode and is expected to remain constant regardless of the bulk concentration in the solution. In the compact layer, the electrostatic forces would dominate the thermal effects and as a result the ions would be, to a first approximation, uniformly packed at a certain maximum concentration, n_{max} , which is a function of only the physical size of the ions and is expected to be constant for a wide range of applied charge and bulk concentration values. The boundary of the compact layer is defined by the location at which the electrostatic force experienced by the ions no longer dominates the thermal effects, and while this depends on the charge density on the electrode, it is expected to be independent of the bulk concentration. Clearly these are approximate ideas, but the key point is that there is a well defined point at which the diffuse layer takes over with a profile determined by simple thermodynamics.

In this diffuse layer, ions are susceptible to thermal agitation since they are not as tightly bound as those in the compact layer. Using the same model of laminae, Equation 2.16 can be used to describe the ion population within each laminae. With this, ϕ_d can be obtained by considering the first lamina at the interface between the compact layer and the diffuse layer. Here, the concentration n must be equal to n_{max} , which is expected to be relatively constant for a wide range of bulk concentration values. Thus, Equation 4.4 shows that ϕ_d has a logarithmic relationship with the bulk concentration. For example, at 300 K for a monovalent anion, this potential is expected to decrease by about 59 mV/decade of bulk concentration increase.

$$\phi_{\rm d} = \frac{-kT}{ze} \ln(\frac{n_{\rm max}}{n^0}) \tag{4.4}$$

Taking into account this offset, it is apparent that for various changes in bulk concentration values, a specific corresponding change of applied voltage is required to achieve the same surface charge density. Since the tunneling model states that the onset of electrochemical reaction depends on the electrode surface charge density, this suggests that varying the bulk concentration would cause shifts in the applied voltage that corresponds to the electrochemical threshold. It is important to note that the expectation of this dependence of the voltage threshold for electrochemical reactions is not new; this is a well known effect¹³. It is however important that this prediction also arose from the perspective of the electron tunneling model presented.

4.2.3 Effect of Surface Roughness

It is well known that virtually all electrode materials have an electrode surface that is not perfectly flat, and this non-flatness generates a non-uniform electric field and therefore a non-uniform local charge density over the electrode surface. Thus, the electron tunneling model allows a more detailed consideration of the effects of surface roughness on the onset of electrochemical reactions. From electrostatics, the charge density tends to be higher around protrusions or bumps on the surface, which are mathematically described as points of convex curvature. Based on the quantum tunneling model presented here, this higher charge density should lead to a higher reaction rate in these regions. This effect is expected to be particularly apparent near the threshold charge level where the local charge density variation has a non-linear effect, which could lead to significantly increased local reaction rates near the protrusions. Because significant electric fields are present only in the double layer, such considerations would only apply to protrusions which are smaller than the double layer, typically on the nanometer scale. This is an important consequence especially in situations where the electrochemical reaction corrodes the electrode, since it can result in the preferential removal of material at the protrusions, leading to nanometer-scale smoothing of the electrode. Characteristics of nanostructured electrodes with respect to electrochemical etching have been studied elsewhere²⁴ and the work presented in this study provided an additional possible application. In some situations, this may be a useful alternative to conventional electropolishing techniques which are not selective at removing only such fine surface features.

4.3 Experimental Verification of the Electron Tunneling Model

Experiments were performed to test each of the above predictions using test cells as depicted in Figure 3.6. Flat electrodes, rather than nanoporous electrodes, were used for these experiments to avoid any extra complexity associated with the complex geometry. Specifically, the test cell comprised of deoxygenated aqueous solution of sodium chloride (NaCl) contained between two electrodes comprised of nominally 20 nm thick ITO films deposited on a float glass substrate¹⁸. The ITO was chosen for its effectiveness as an optically transparent electrical conductor.

4.3.1 Experimental Measurements of the Threshold Voltage and Charge

The key hypothesis derived in the previous section is that the accumulated charge would be the best predictor of the onset of electrochemical reactions under transient conditions. In the experimental study, the effects of the applied voltage and the applied surface charge were separated using a sinusoidal time-varying applied voltage from a digital function generator²⁵, so that the desired magnitude of charge could be deposited on the electrode without the need for a persistent applied voltage. The frequency of the applied signal was varied between 20 and 100 Hz. The voltage was applied across a test cell with 1.0 M NaCl solution to induce electrochemical reaction. The rate of electrochemical activity was monitored by measuring the change in the resistance of one of the ITO electrode over time. This was determined to be an accurate way to measure the electrochemical activity since the reaction that occurred had been known to irreversibly damage the surface of the ITO by chemical degradation, thereby increasing the resistance of the conductive layer.

Figure 4.5 shows the circuit that enabled real-time measurement of the DC resistance of the ITO electrode while the alternating current (AC) voltage induces the electrochemical reactions. The resistance was calculated by measuring the current induced by a 50 mV DC probe voltage applied across the two ends of the electrode using a DC power supply. The AC and DC signals were kept separated using capacitive and inductive components. The measured current itself was amplified and converted to a voltage signal with a large dynamic range amplifier²⁶ before digitization and recording.



Figure 4.5. Schematic of the circuit for real-time electrode resistance measurement.

To maintain a well-defined charge level, the amplitude of the voltage applied between the electrodes was kept sufficiently low (<5 V) that any current associated with electrochemical reactions was much lower than the charging current. Thus the applied charge to the effective double layer capacitance was simply the time integral of the current.

When the magnitude of the applied AC charge was increased to the point that an increase in the electrode resistance was observed, the resistance typically increased at an approximately constant rate, which was consistent with the electrode gradually being etched away since the electrical conductivity of the layer can be expected to be proportional to its thickness. While the specific reaction that took place was not clearly known, but others²⁷ have noted the electrolysis-based deterioration of ITO thin films and attributed it to reduction of the film to metallic indium. To quantify this rate, the resistance was measured over a ten minute period during which a constant-amplitude AC current was applied, and the rate of change of the electrode resistance remained close to zero up to a certain amplitude threshold of the applied AC current (that depended on the frequency), after which the rate

increased rapidly, as shown in Figure 4.6. (Of course, as the current increased, so did the voltage, but the relationship between voltage and charge was more complex because the impedance of the overall circuit was frequency dependent.) To estimate this threshold value, the data was fitted using a combination of two different linear relationships, one in which the resistance change rate was zero up to a particular threshold value, and a second that increased linearly for all values exceeding this threshold value. If, as our model had suggested, the factor that precipitated a non-negligible electrochemical reaction rate should be the accumulation on the electrode of a critical surface charge density, then a simple prediction should result: The required RMS cell current to achieve this required peak surface charge density should be proportional to frequency, and the peak charge density itself should be independent of the frequency of the applied RMS cell current. Figure 4.7 depicts the former case by plotting the RMS cell current at the threshold of electrochemistry vs. frequency, showing the predicted linear relationship, and Figure 4.8 shows the constancy of the threshold charge with respect to frequency. Both of these plots show results consistent with the model.



Figure 4.6. Typical evolution of the electrode resistance change rate for increasing RMS cell current.



Figure 4.7. The threshold RMS cell current at different applied current frequencies.



Figure 4.8. The threshold maximum double layer capacitive charge at different applied current frequencies.

4.3.2 Effect of Bulk Concentration on the Threshold Voltage

In order to observe the predicted shift in the threshold voltage for electrochemical activity for different bulk concentrations, the rate of electrochemical reaction at different applied voltage levels was measured using a staircase voltammetry technique¹³. A sequence of increasing DC voltage levels resulting in a staircase profile was applied between the electrodes using an analog output on a data acquisition card²⁸. The duration of each voltage step was chosen to

be 20 s, sufficiently long that the capacitive double-layer charging current was allowed to settle prior to measuring the electrochemical reaction current at that particular voltage.

Since the concentration saturation point at room temperature for an aqueous NaCl solution is about 6 M, experiments were performed with solutions with concentration values ranging from 1.0×10^{-3} M to 1.0 M, covering three orders of magnitude. The minimum concentration value was selected because for any lower concentration the high resistance of the bulk solution and the effects of impurities introduced significant error. The maximum concentration was selected to avoid saturation.



Figure 4.9. Electrochemical current for different bulk NaCl solution concentrations plotted against (a) the cell voltage and (b) the cell voltage corrected by the expected 59 mV/decade of concentration offset.

It may be helpful to point out that the bulk electrolyte concentrations were very different than the ionic concentrations found near the electrode, where the species attracted to the electrode can have a very high local density. At such high densities, activity effects would be important and would have to be taken into account in a full and detailed treatment. In the comparisons in this experiment, however, we were selecting voltages that produce comparable reaction rates, which presumably correspond to similar concentrations at the electrode. Thus the primary differences in the ionic distributions under such similar electrode conditions occurred in the low density "tail" of the distribution far from the electrodes, and it was the voltage differences in those regions that was observed and was expected to relate directly to the bulk electrolyte concentration.

Over this thousand-fold range of concentration, the predicted shift of the threshold voltage with increasing bulk concentration was observed (Figure 4.9a). By shifting the applied voltage to correct for the predicted increase in threshold voltage of 59 mV/decade of concentration, the curves overlapped almost identically, as shown in Figure 4.9b. Overall, the results showed good quantitative agreement with the model.

4.3.3 Measurements of the Preferential Removal of Electrode Material

The non-uniformity in the reaction rate across the surface of a rough electrode was expected to be most apparent near the threshold point at which electrochemical reactions would begin to occur, since this condition would be favorable for reactions at the surface protrusions but not at all in other regions. To observe this effect, a series of three experiments were performed in which a test cell containing 1.0 M NaCl solution was maintained under an applied DC voltage of 1.6 V for three different time periods: 0.5 hours, 2.0 hours and 17.0 hours. The surface topography of the anodes, for which macroscopic changes had occurred in earlier trials, was then observed using a Digital Instruments Nanoscope atomic force microscope (AFM) in tapping mode. Since the predicted phenomenon was expected to only affect features whose size was comparable to the nanometer-order Debye length, the scans were processed with a Gaussian high pass filter to isolate features of this size.



Figure 4.10. Atomic force microscope scans of anode surface for (a) an unexposed sample, and samples that have been etched for (b) 0.5 hours, (c) 2.0 hours, (d) 17.0 hours.

Comparing the scans in Figure 4.10, it is apparent that the height of the protruding bumps decreased as the reaction time increased. Since only the regions with protruding bumps were expected to be affected and the fraction of these regions in the overall scan area was not controlled across different scans, a comparison of the RMS roughness was insufficient to identify consistent change across multiple scans. Instead, to quantify this change, the regions with protruding bumps were first identified as points having two negative principle curvatures. Then, the mean principle curvatures of these points were calculated and averaged for all such points on the scan, so that this average can be compared against values for each of the samples. The rounding of these bumps would be indicated by this average mean curvature becoming less negative. Figure 4.11 shows the average of the mean curvature of these points for each scan compared to that of an unexposed sample. The smoothing effect was found to increase as the reaction time increased, as predicted by the model.



Figure 4.11. The decrease in average mean curvature for points of convex curvature in atomic force microscope scans of anode surface after different etch times.

4.4 Decreasing Transition Time of Electrophoretic Ionic Optical Devices

With all three predictions verified by observations, the results presented thus far were applied to significantly decrease the transition time for electrophoretic ionic optical devices by more quickly moving dye ions into and out of the pores of a nanoporous electrode while avoiding electrochemical reactions. While electrophoretic ionic optical devices have been shown to be operational when employing minimal voltage levels (sufficiently low to avoid electrochemistry), the time required for the transition between two different optical states was on the order of seconds, which was unacceptably long for many applications. Rather than limiting the voltage, if instead the accumulated charge on the electrode was maintained below the predetermined threshold value for electrochemistry, then the model predicted that the maximum applied voltage could be substantially increased, if only for a short period of time. For example, a pulse at 50 V could be applied to rapidly move the dye ions and then a maintenance voltage of less than 1 V could be applied to maintain the device in that optical state.

4.4.1 High Speed Drive Circuit



Figure 4.12. Electrical Schematic of the high speed drive circuit.

To accomplish this drive voltage scheme, a simple high speed drive circuit consisting of capacitive and resistive components, shown in Figure 4.12, was used to apply the desired voltage vs. time profile to an electrophoretic ionic optical device. When a high amplitude square wave voltage was applied to the input of this circuit, the circuit yielded a cell voltage vs. time profile that consisted of a short pulse at the high voltage that rapidly decayed, in an exponential fashion, to a constant steady state voltage of about 1/50 of the input voltage

amplitude (Figure 4.13). The rate of decay was related to the ratio of the external capacitor and the overall electric double layer capacitance of the test cell.



Figure 4.13. High speed drive circuit output cell voltage profile with a 15 V step input voltage.



Figure 4.14. Optical setup of TIR reflectance test used to evaluate the absorption modulation in an electrode of an electrophoretic ionic optical device.

The electrophoretic ionic optical device tested in this case consisted of two transparent nanoporous $ZnSb_2O_6$ electrodes submerged in 1.73×10^{-4} M MB-methanol solution. The $ZnSb_2O_6$ films used were nominally 800 nm thick. To focus the probing to the

region within or close to an electrode, the optical properties of the charged $ZnSb_2O_6$ was observed by measuring the intensity of a light beam reflected from the test sample by means of TIR. This was achieved by directing the beam of a 3 mW, 650 nm wavelength laser diode on one of the electrodes in the sample through an acrylic coupling prism placed in optical contact with the glass substrate of the sample using type A immersion oil, in order to ensure the correct angle of incidence, as depicted in Figure 4.14. The incident wavelength was chosen due to its proximity to the absorption peak of the MB dye. This was the standard reflectance test setup used throughout this study.

For these measurements, the incident angle was chosen to be 68.4° , which for a glass/methanol interface exceeded the critical angle for TIR of 61.2° . Given that the real component of the refractive index of ZnSb₂O₆ is given by the manufacturer as 1.70, the effective refractive index of the methanol-impregnated nanoporous layer was expected to be higher than that of glass, so that the laser light would propagate through the nanoporous layer wherein absorption occurred before and after experiencing TIR as it encountered the bulk solution. The intensity of the reflected laser beam was measured by directing the reflected beam into an integrating sphere containing a silicon photodiode detector, whose signal was amplified through a large dynamic range amplifier²⁶. When the dye ions were moved by electrophoresis into the porous electrode structure, the imaginary component of the local effective refractive index substantially increased, and consequently the reflected signal was attenuated as observed by a decrease in the intensity of the reflected light. For this test, a relative measure was sufficient to establish transition time and possible electrode decay. Detailed measurement of the degree of absorption that took place within the ZnSb₂O₆ layer is discussed in Chapter 5.

As a control case, the results obtained when using the high speed drive circuit was compared to that obtained when using a simple circuit, where a low-amplitude square wave from a function generator²⁵ was directly applied to the electrodes. In both cases, an offset square wave was used for the input voltage, where it would be 0 V for half of every period, so that the system returned to the fully discharged state between every charge. A period of 100 s was chosen for the square wave, since the system required up to 20 s to reach steady state with an applied voltage of less than 1 V (Figure 4.15). For the high voltage required for

the high speed drive circuit, the square wave signal from the function generator was used to control the output of a bipolar operational power supply²⁹ to have a maximum amplitude of up to 50 V. For comparison between different cells and voltages, all reported intensities were normalized by the intensity measured when the system was in the fully discharged state.



Figure 4.15. Intensity modulation of reflected light with application of a simple 0.01 Hz square wave voltage with various amplitudes.

4.4.2 Reflected Beam Intensity Modulation Profiles

Comparing the reflected beam intensity modulation profiles obtained with the simple and the high speed drive circuits, using approximately the same steady state cell voltage, the response immediately after switching was much faster in the high speed drive circuit both during charging and discharging, while similar magnitude of optical change was seen for

both circuits (Figure 4.16). The peak response during charging was achieved in as little as 0.1 s (Figure 4.17).



Figure 4.16. Comparison of intensity modulation of reflected light with the simple circuit and the high speed drive circuit, both with steady state voltage of 0.5 V.



Figure 4.17. Intensity response immediately after switching to the on-state with the high speed drive circuit.



Figure 4.18. Intensity modulation of reflected light with application of 0.01 Hz square wave voltage using the high speed drive circuit with various steady state voltages.

As well, the peak response was observed to be voltage-dependent, with higher applied voltage resulting in a higher peak response relative to the steady state response (Figure 4.18). Furthermore, this magnitude of the intensity change would decrease after the peak and slowly increase again. Even though it was not completely understood how this came about, this might be related to the time dependent capacitance of the nanoporous electrodes due to higher resistive shear forces deep within the pores and also the finite time required to reach those deeper regions. Effectively, only a certain portion of the electrode area was available during the time of the high voltage pulse from the high speed drive circuit. Therefore, the capacitance during that time was lower than that in the steady state. As the cell voltage dropped towards the steady state voltage, the level of charge dropped to a certain level but then slowly increased as the capacitance increased over time, when the deeper pore regions became available. This effect would likely have a complicated dependence on voltage, since higher voltage would increase the total overall charge, so more dye ions would need to reach the regions deep within the pores, but at the same time, higher voltage would induce higher electric field to overcome the shear forces and reduce travel time. Presumably a more complex driving scheme could be implemented to create a smoother transition.
Nonetheless, these results successfully showed that these devices could withstand a high applied voltage for a short period of time, consistent with the electron tunneling model, and that such high voltage could greatly improve the response time of these devices.



4.4.3 Long Term Cycling Measurements

Figure 4.19. Evolution over time of the relative change in steady state reflectance ("contrast") of an electrophoretic ionic optical device as it is cycled at 0.01 Hz at different steady state voltages with the simple circuit and the high speed drive circuit.

In addition to achieving the same optical effect within a shorter time, it was also necessary to demonstrate that the lifetime of the device would not be compromised by the use of the high speed drive circuit. To this effect, a cell was cycled with a 0.01 Hz square wave for 8 hours at various steady state voltages. The simple and high speed drive circuits showed comparable results (Figure 4.19). For both the 0.3 V and 0.5 V cases, no noticeable change in the contrast (defined as the reflectance in the steady state off state divided by the reflectance in the steady state on state) was observed. Note that for the 0.5 V high speed case, the cell was exposed to short pulses of as high as 25 V; if this voltage were applied for an extended period of time to the cell, the cell would have been rendered inoperative within seconds. For the 1.0 V cases with both the simple and high speed drive circuits, the contrasts

were observed to approach unity over time, implying less effectiveness in increasing the absorption properties of the electrodes. This was inconsistent with the measured electrochemical threshold of 1.2 V. Nonetheless, it should be noted that after leaving the system in the uncharged state over 48 hours, the contrast returned to the initial level. Therefore, this last observation could be interpreted as either reversible electrochemical reactions or ion buildup within the pores over many cycles due to the lack of applied voltage to discharge the system. Despite that, the decay rate observed when using the high speed drive circuit was comparable to that when using the simple circuit.

To determine if ions were simply building up within the pores due to the lack of applied voltage to discharge the system, the 1.0 V steady state voltage case was repeated with a bipolar input voltage that switches between +50 V and -50 V, instead +50 V and 0 V. It was observed that this forced discharge indeed eliminated the contrast decay. Therefore, it was likely that the decay in optical performance was due to asymmetric charge and discharge voltages, resulting in ion buildup within the pores over many cycles, and not due to electrochemical reaction. It therefore seems reasonable to expect that the use of steady state voltage up to 1 V and a maximum applied voltage of 50 V would not appreciably damage the electrodes.

The above two results further validated the electron tunneling model in that it was possible to apply a high voltage for a short time to achieve the same optical change with a significantly shorter response time in electrophoretic ionic optical devices. Due to the short time of the pulse, the charge level was kept low in order to prevent undesirable irreversible electrochemical reactions, therefore maintaining the lifetime of the device. The response time was reduced from 5 s to 0.1 s. The development of the electron tunneling model had enabled significant optimization in the response time and lifetime of electrophoretic ionic optical devices.

5 OPTICAL PROPERTIES OF PROTOTYPE MATERIALS

In order to effectively model the variable diffraction grating, it was important to accurately determine the complex index of refraction for each of the material involved. While published values could be found for the indices of the glass substrate and the ITO layer, the other indices needed to be determined through measurements. During this study, the indices were only measured for the wavelength of 650 nm, as this was the wavelength at which the prototype was tested. For the MB solution, a direct measurement by transmission was done. For the nanoporous ZnSb₂O₆, to focus on the region within and near the electrode, the refractive index as well as the porosity was determined by matching the measured reflectance off of the electrode at a series of angles with results from an appropriate simulation using the GSolver® rigorous coupled-wave analysis software package (Appendix A).

5.1 Methylene Blue Dye Solution

Since the MB-methanol electrolyte used during this study had relatively modest concentration, the volumetric fraction of the MB dye within the methanol solvent was not expected to noticeably affect the real component, $n_{\rm R}$, of the complex index of refraction of the electrolyte. On the other hand, it was expected that the imaginary component, $n_{\rm I}$, of the complex index of refraction would be directly proportional to the dye concentration for modest concentration, since methanol is transparent at the wavelength of interest.

5.1.1 Complex Refractive Index Measurement Procedures

The $n_{\rm I}$ of the MB-methanol solution was measured at different concentrations by measuring the transmittance through a layer of solution 0.16 mm thick at normal incidence contained within a cell made up of two 25 mm × 25 mm × 1 mm glass slides. The thickness was set by using 0.16 mm thick glass microscope cover slides sandwiched between the glass slides. The sides of the cell were then sealed with epoxy, while the top and bottom were left open to insert the electrolyte (Figure 5.1). The spacing between the two glass slides was small enough that the surface tension was sufficient to prevent the liquid from draining out the bottom. A perfect seal was not required as the time needed for the tests was sufficient short compared to the rate of evaporation of methanol at room temperature. To account for partial reflections between the glass-air and glass-electrolyte interfaces, the measured intensity was normalized by the intensity measured when the cell was filled with pure methanol, given that the n_R of the solution was approximately the same as pure methanol.



Figure 5.1. (a) Side cross-section and (b) front view of a test cell containing a thin layer of dye solution for transmittance measurements.

5.1.2 Complex Refractive Index Measurement Results

Figure 5.2 shows the measured n_1 of the MB in methanol solution at different concentrations spanning three orders of magnitude. The linear fit model was consistent with the measured data. The constant of proportionality that relates the concentration of dye with the measured n_1 was determined to be 0.93 M⁻¹.



Figure 5.2. Log-log plot of the imaginary index of refraction vs. MB dye concentration in methanol solution, fitted line shows a transformed linear function.

5.2 Zinc Antimonate Nanoporous Electrodes

For the ZnSb₂O₆ nanoporous electrodes, a TIR reflectance test was used to focus the measurement to a region within or near the electrically conductive thin film. An additional variable to consider was the porosity of the nanoporous electrodes. This was inferred by measuring $n_{\rm R}$ and using effective medium analysis from test results when the pores were filled with methanol and with air. The method benefited from the sharp rise in reflectance as the incident angle approached the critical angle, which in turn was strongly dependent on the effective $n_{\rm R}$. By comparing the measured results with different GSolver® models, it was possible to also determine the $n_{\rm I}$ of the bulk ZnSb₂O₆ as well.

5.2.1 Complex Refractive Index and Porosity Measurement Procedures

A reflectance test (Figure 4.14) was done with nominally 800 nm thick $ZnSb_2O_6$ thin film deposited on ITO-coated glass substrate. The reflectance was measured at a series of different incident angles, θ_i , beyond the critical angle of a glass-air interface (41.2°), such that the case of 100 % reflectance at the interface could be defined by similar measurements with a glass slide exposed to air at these angles. Measurements were taken with the thin film exposed to air and with the thin film submerged in pure methanol. GSolver® models with no periodic features were constructed to predict the reflectance off of an unpatterned thin film with an linearly p-polarized incident beam. The effective n_R and n_I of the nanoporous layer in the model were varied until a reflectance curve was obtained that was consistent with the measurement. From this effective n_R and n_I , effective medium analysis was applied to deduce the porosity and the n_I of the bulk ZnSb₂O₆, using the n_R of 1.70 for bulk ZnSb₂O₆ given by the manufacturer and a n_I of 0 for both air and methanol.

5.2.2 Complex Refractive Index and Porosity Measurement Results

Consistent models were constructed for both the air case (Figure 5.3) and the methanol case (Figure 5.4). The sharp rise in reflection near the critical angle was particular useful in determining the effective $n_{\rm R}$ of the ZnSb₂O₆/methanol layer. The models were also consistent with each other, as the both of these gave film porosity of 0.34 (i.e. the film was 66% ZnSb₂O₆) and bulk ZnSb₂O₆ $n_{\rm I}$ of 0.0041. These results were important for the determination of the amount of dye within the nanoporous layer.



Figure 5.3. Measured reflectance of a 800 nm thick $ZnSb_2O_6$ layer in air compared to the predicted reflectance of a layer with n_R of 1.45 and n_I of 0.0026. The incident angle corresponds to θ_i in Figure 4.14.



Figure 5.4. Measured reflectance of a 800 nm thick $ZnSb_2O_6$ layer in methanol compared to the predicted reflectance of a layer with n_R of 1.57 and n_I of 0.0032. The incident angle corresponds to θ_i in Figure 4.14.

5.3 Methylene Blue Dye within Zinc Antimonate Nanoporous Electrodes

Combining the above results for MB dye and ZnSb₂O₆, it was possible to predict the absorption properties of the nanoporous electrodes for samples containing different concentration of the dye. However, since the movement of the dye ion and the chlorine counter-ion both contributed to the overall measurable accumulated charge, and considering that these ion species may move at different speeds, it was not clear what concentration corresponded to a specific charge level. Moreover, it was also observed that even without any applied voltage between the two electrodes the dye concentration within the pores was significantly higher than the bulk dye concentration, especially when the bulk concentration was low. To explore these phenomena, the absorption properties of the nanoporous layer were measured at different concentrations and different applied voltages. Finally, it was also suspected that the absorption properties of the dye might change as it entered the nanoporous layer due to the changing electrical environment, so the transmission through one of the two electrodes and a thin layer of bulk solution was measured to verify that this was not the case.

5.3.1 Dye Concentration within Nanoporous Conductor

To see the dye concentration within the pores, a reflectance test was performed at different applied DC voltage values and bulk concentrations with test cells comprised of two $ZnSb_2O_6$ films. The results were then fitted with a GSolver® model to obtain the effective n_1 . Again, effective medium analysis was used to determine the n_1 , and thus the dye concentration via the results from Section 5.1, of the solution within the pores. Given the good agreement with model from the methanol case, these tests were only done at a single incident angle.

It was found that the concentration within the pores of the uncharged cell was higher than that in the bulk solution. This was attributed to the significant surface area of the nanoporous layer, within which high percentage of the pore volume was part of the monolayer immediately outside the electrode. From energy arguments, it could be expected that both types of ions might have lower average energy near the surface, effectively increasing electrically neutral combination of dye ion and counter-ion concentration within the nanoporous electrodes. The results were qualitatively consistent with this model.

With an applied voltage, the dye concentration changed linearly. Nonetheless, the change in absorption could only account for a small percentage of the accumulated charge in the electrodes. This was thought to be due to one or both of two key factors. First, the significant difference in size between the dye ions and the chlorine counter-ions might let the counter-ions move faster and also more readily access electrode surface deep within the nanoporous electrodes, so that the presence and absence of counter-ions made up the majority of the accumulated charge on the electrode. Alternatively, the absorption properties of dye might weaken within the porous electrode due to significantly different electrical environment. To distinguish which was the case, a test to observe this deactivation of dye was performed.

5.3.1.1 Complex Refractive Index Measurement Procedures

A series of reflectance tests (Figure 4.14) were performed using two 800 nm thick $ZnSb_2O_6$ nanoporous thin film containing MB dye electrolyte of various concentrations. To reduce

error in laser placement and sample surface non-uniformity, a single cell was used for all the uncharged cases and another was used for all the charged cases without dissembling the cell. Dye solutions were tested in increasing concentration to avoid contamination through successive tests. The tests were performed at an incident angle of 68.4° , which was well beyond the critical angle of the glass-methanol interface. The resulting reflectance was determined again by normalizing the measured intensity with that from a similar measurement for a glass-air interface. The effective n_1 was inferred by generating GSolver® model results that fitted well with the measured reflectance at that orientation. The applied DC voltage magnitude was kept below 1 V to avoid inducing electrochemical reactions.

5.3.1.2 Complex Refractive Index Measurement Results

In the absence of an applied voltage, it was observed that the concentration required to achieve the measured absorption was higher than expected for a given bulk concentration (Figure 5.5). This effect was especially apparent for systems with low bulk concentration, while the two converged at high bulk concentration. This was consistent with the idea that both types of ions within the electrolyte favored being within the monolayer immediately outside the electrodes, resulting in an increase in optical absorption but still an overall neutral charge. This effect was expected to saturate at higher concentration, as observed.



Figure 5.5. Imaginary refractive index as measured within the porous conductor compared with that expected in the bulk solution.

When a voltage was applied across the two electrodes, the dye concentration varied linearly from the uncharged concentration with the applied voltage at a rate that was largely independent of the bulk concentration (Figure 5.6). Thus, optical changes could occur by charging the electrode with dye ions or by discharging the electrode of the initial dye ions present. At low bulk concentration, it was possible to completely push out all the dye from within the pores, as in the 1.73×10^{-5} M case. Interestingly, as the dye was completely pushed out, the other electrode symmetrically experienced resistance pulling more dye in, creating non-linear response for the cases of 1.73×10^{-5} M with the applied voltage magnitudes larger than 0.4 V. To maximize the fractional difference of the complex refractive indices of the two electrodes, it was desirable that the dye concentration within the electrode that was pushing out dye ions would just reach zero when charged to 1 V. This occurred at a bulk concentration. Table 5.1 summarizes all the n_R and n_I used for modeling the prototype, including the ones determined through the tests described above.



Figure 5.6. Imaginary refractive index of the electrolyte within the nanoporous electrode at various applied voltages and various bulk concentrations.

It should also be noted that the measured concentration change only corresponded to less than 6% of the total charge, as found by integrating the charge current. This could be attributed to the significant difference in size between the MB dye ion and the chlorine counter-ion, leading to significantly larger electrophoretic mobility for the smaller counterion. At the same time, it was also possible that the absorptive properties of dye ions would decrease as the dye moved into the pores. Therefore, a test was devised to determine if this was the case.

Material	n _R	nı
Glass	1.517	0
Acrylic	1.490	0
ITO	1.775	1.2×10 ⁻²
1.73×10 ⁻⁴ M MB-Methanol Electrolyte	1.329	1.9×10 ⁻⁴
ZnSb ₂ O ₆ Electrodes at +1 V	1.570	1.4×10 ⁻²
ZnSb ₂ O ₆ Electrodes -1 V	1.570	3.5×10 ⁻³

Table 5.1.	Complex refractive indices of materials used for modeling the prototype
	grating.

5.3.2 Dye Deactivation Test

Based on the above results, it was suspected that the dye may "deactivate" its absorptive properties as it entered the nanoporous conductor, since the electrical environment there could be very different from that in the bulk solution. To verify if this was the case, the transmittance through one of the two electrodes and a thin layer of solution was measured as the system charges and discharges. Given that the n_1 is proportional to the dye concentration and that the transmission loss increases exponentially with the layer thickness, the overall transmittance is suspected to be independent of the specific distribution of the dye along the propagation direction, as long as the absorptive properties of each dye ion and the number of dye ions that the light passes through do not change. However, if this "dye deactivation" indeed occurs, then as the dye ions move from the bulk solution to within the nanoporous conductor, the transmittance would increase. No change in transmittance was observed, thus enabling us to discard this hypothesis.

5.3.2.1 Dye Deactivation Observation Procedures



Figure 5.7. Optical setup of the dye deactivation test.

In attempting to see the expected effect, it was important to transmit the light beam through only one electrode but at the same time maintaining the ion movement to be along the propagation direction. Test cells similar to the ones shown in Figure 5.1 were constructed, except the glass slides were replaced with 800 nm think ZnSb₂O₆ thin films on glass substrates, and that copper wires were connected using silver conductive epoxy¹⁹ to make the A 1.73×10^{-4} M MB-methanol solution was used. necessary electrical connections. Moreover, a roughly 1 mm \times 1 mm window was scratched off in one of the ZnSb₂O₆ thin film for the incident light to pass through (Figure 5.7). The window area was small compared to the overall area that the electrode was exposed to the electrolyte, so that the ion movement could still be expected to travel in a direction normal to the electrode surface near the other electrode. The 650 nm wavelength laser beam was focused using a 35 mm focal length (FL) converging lens into the 1 mm \times 1 mm window, and then re-collimated into an integrating sphere with a 45 mm FL converging lens. The transmittance was monitored as a 0.05 Hz square wave that switched between 0 V and +1 V, as well as one with 0 V to -1 V, was applied across the electrodes. This was done so measurements were obtained for both cases where the electrode being measured would be pushing out dye or pulling in dye. In both cases, the electrode with the window would be connected to ground.

5.3.2.2 Dye Deactivation Observation Results

The overall transmittance level was consistent with the measured n_1 values, where the bulk solution was expected to absorb about 40 % of the incident beam intensity through this thickness and then the electrode would absorb 3 to 12 % of the initial intensity. No significant change in transmittance was seen as dye was moved from the bulk solution into the electrode (Figure 5.8a), contrary to the hypothesis. For the case where the dye was pushed out of the electrode, there was significant increase in transmittance observed (Figure 5.8b). This asymmetry was attributed to the movement of ion around the window in the electrode which the light does not pass through. While the electrode being measured was pushing out dye, the other electrode was pulling in dye. Even though the small window could sufficiently ensure that the ion movement near the electrode being measured was approximately normal to the thin film, this was not expected in the region around the window. Therefore, dye ions within the window region were being pulled perpendicular to the light propagation direction and out of light beam path as the electrode material around it pulled dye in, thus increasing the overall transmittance. As such, the case where dye was pulled into the measured electrode was expected to be more representative. Thus, it could be concluded that no significant change in absorption properties of the dye ion occurred as the ions entered and exited the nanoporous electrode.



Figure 5.8. Transmittance through a thin layer of dye solution and a nanoporous thin film electrode that is (a) pulling in dye and (b) pushing out dye.

6 VARIABLE DIFFRACTION GRATINGS

Electrophoretic ionic optical devices can have a wide variety of possible electrode arrangements for use in various applications. For the purpose of this study, it was desirable to focus on a specific design of a variable diffraction grating. Such a grating can be made by creating a series of lines of nanoporous conductor, so that the period of the grating can be altered by selectively darkening certain lines by electrophoresis. As a proof-of-principle prototype, a device was designed that would be able to switch between two distinctly different patterns. In this chapter, the working principle of the prototype is explained and the major design features are discussed.



6.1 Interdigitated Electrodes as Variable Diffraction Gratings

Figure 6.1. A variable diffraction grating implemented as two interdigitated electrodes in (a) its uncharged state and (b) its charged state.

As explained in Section 2.3, the deflection angle of the diffractive order depends on the period of the grating. By increasing the period, new diffractive orders can be introduced to direct the outgoing beam into different directions. One way to accomplish this is to pattern two electrodes in the form of interdigitated electrodes (IDEs), thus named because they look like two sets of fingers interlaced with each other. In the uncharged state, the set of lines would behave as a diffraction grating of a certain "uncharged period" (Figure 6.1a). By applying a voltage bias between the two electrodes, dye ions would be attracted to one of the electrodes and therefore would darken certain lines in the grating. This would increase the period of the grating to the "charged period" (Figure 6.1b), and would change the diffractive pattern as a result. Of particular interest are gratings with an uncharged period that is submicron in size. With such a grating, it would be possible to find incident geometries that only have a 0R diffractive order when used with visible light, which behaves like the reflected beam off of an unpatterned optical interface. When such a system is charged, the period of the grating would increase well beyond the wavelength of the light and thus would generate one or more new deflected diffractive orders to redirect some of the light into a different directions (Figure 6.2).





Figure 6.2. Schematic representation of diffractive orders of a sub-micron pitch variable diffraction grating in its (a) uncharged state and (b) charged state.

6.2 Charging Behavior of Interdigitated Electrodes

The geometrical setup of the IDEs introduces two further complications to the electrical behavior of the system. First, the electric field between the two electrodes can no longer be approximated as uniform, since different parts of the electrodes are at vastly different distances from the other electrode. Second, the small cross-sectional area of the fingers of the electrodes introduces significant resistances and therefore a significant voltage drop and non-uniform charge distribution along each finger whenever current flows through the system.



Figure 6.3. Schematic representation of electric field between two fingers of a set of IDEs.

To consider the non-uniformity of the electric field, let us assume the electrodes to be perfect conductors with zero electrical resistance, so that they would each be at the same electrical potential throughout. Also, we only consider the instant immediately after voltage has been applied, when the electrical double layers do not bring about significant shielding effects. The electric field strength, \vec{E} , between the two electrodes would be related to the potential difference, ΔV , between them by the following equation:

$$\Delta V = \int_{S} \vec{E} \cdot d\vec{s} \tag{6.1}$$

where S defines a path from the surface of one electrode to the surface of the other. Qualitatively, larger the separation between the two electrodes would mean weaker electric field strength along those paths. Thus, the field would be the strongest within the gap that separates the two electrodes (Figure 6.3). Away from this gap, the electric field would have to penetrate further into the electrolyte and to take a longer path to achieve the same potential difference, so the electric field would be increasingly weaker in these regions. During electrophoresis, this would cause the dye to be attracted to regions of the electrodes closest to the gap first. Since the separation between the two electrodes is small everywhere within the IDEs, this would likely lead to the IDE fingers optically responding faster than the unpatterned parts of the electrodes. Also, since the separation between the IDEs are much smaller, this is expected to exhibit improved response time compared to two unpatterned electrodes placed far apart.

On the other hand, because of the long shape of each IDE finger, the IDE fingers can have a significant electrical resistance. The resistance, R, of an object with uniform cross-sectional area, A, and length, l, can be given by its resistivity, ρ .

$$R = \frac{\rho l}{A} \tag{6.2}$$

The ratio l/A tends to be large for the IDE fingers, giving rise to significant resistance. During normal operation of the variable diffraction grating, this can affect the transient charging profile, but since no current is expected to flow during steady state, this increase in resistance should not affect the overall charge. However, if the applied voltage is high enough to induce electrochemical reaction, the steady state current would not zero and in this case the voltage drop along the finger would reduce the amount of charge held by the tip of the finger, relative to that which would take place in the absence of such resistance.

To observe these predicted effects, a pair of large-scale IDEs was tested in reflection with a slightly modified setup, which still involves a test cell whose glass substrate was in optical contact with an acrylic prism using of type A immersion oil. The large-scale IDEs were made by hand-scribing a zigzag pattern, using a diamond scribe, into the $ZnSb_2O_6$ film with a period of roughly 1 mm. To observe the reflectance modulation over a larger area, a collimated beam of white light with a beam width of 6 mm was used. The resulting image was shone through a piece of scotch tape which served as a diffusing screen (Figure 6.4).



Figure 6.4. Reflectance test setup for large scale IDEs.



Figure 6.5. Reflectance attenuation of a large-scale IDEs for different applied DC voltages.

The observations were consistent with the prediction (Figure 6.5). As the applied DC voltage increased, the dye movement started along the fingers where more of the electrode volume was physically near the other electrode. As the voltage became sufficiently high to induce electrochemical reaction, the dye began to drain way from the tips of the IDE fingers. These results motivated the prediction that the response time of the active diffraction grating would be significantly shorter than in the case of two unpatterned electrodes placed 10 mm apart as tested before. Also, this further highlighted the importance of not causing electrochemical reaction, irreversible or otherwise, since the presence of faradaic current reduces the ability of the tips of the IDE fingers to hold charge.

6.3 **Proposed Prototype Pattern**

Based on the above discussion, it was required that a nanoporous thin film be divided into two IDEs. The incident light was again provided by a 3 mW, 650 nm wavelength laser diode, which was linearly p-polarized using a linear polarizer sheet. The dimensions of the grating were set by ease of fabrication and testing, and efficiency arguments, since the focus was placed on the successful fabrication of a proof-of-principle device. The performance and optimal orientation of the designed grating was predicted by modeling with a rigorous grating analysis software package called GSolver® (Appendix A). Indeed, the dimensions of the individual fingers could be further optimized, if the fabrication method had allowed, to give higher diffractive efficiencies. This was explored through a series of GSolver® models.

6.3.1 Overall Grating Design

To provide a sufficient number of lines and a large enough area for a laser beam to focus on, the size of the overall grating was designed to be 40 μ m × 100 μ m (Figure 6.6). One side was longer to better accommodate the beam, since the incident beam needed to hit the grating at a fairly high incident angle necessary to ensure TIR. Also for efficiency, it was decided that every third line of the grating would be darkened in order to reduce the fraction of the darkened area when the system was charged and therefore minimizing the light lost due to absorption. This set the charged period at three times the uncharged period. While darkening every fourth lines would further decrease the fraction of the dark area, it would

also increase the charged period and reduce the achievable deflection angles of the resulting device. Finally, if all the IDE fingers have the same length, the patterns at the ends of the grating would introduce features that are at the charged period even in the uncharged state, which would in turn result in an uncontrolled component to the -1R diffractive order. Thus, the ends of the grating were made into a diamond pattern so that even the ends of the uncharged grating had no features that repeated at the charged period, in order to preserve a high signal contrast.



Figure 6.6. Proposed prototype grating design showing the diamond end pattern, the shaded region represents the dye-rich electrode. The grating line period is not drawn to scale.

For the prototype, fingers with rectangular cross-sections were used as it was the simplest to fabricate. Similarly, the fine features of the grating were largely constrained by

the capability of the fabrication techniques. For prototyping, the focused ion beam milling technique was used (see Chapter 7). To obtain high deflection angles from the grating, it was important to have the uncharged period as small as the fabrication technique would allow. Due to possible damage to the nanoporous layer, this was limited to be about 667 nm, giving a charged period of 2.00 μ m. Similarly, although a thicker grating allows more dye to interact with the light, the thickness could not be too great, as this would involve fingers with too high an aspect ratio that individual fingers may be unstable mechanically. As well, the depth of a cut was also limited by the possibility of damaging the nanoporous layer. Therefore, a ZnSb₂O₆ film with a thickness of 800 nm, grown on ITO coated glass slides, was used.

6.3.2 Predicted Performance of the Designed Grating

In order to predict the performance of the designed grating, a simple rectangular model of the grating was constructed in GSolver®, where one out of three fingers was darkened (see Appendix A). The complex refractive indices used were based on measurements presented in Chapter 5. The incident beam was set to be linearly p-polarized. The model was used to predict performance for a range of incident orientations within the glass substrate, specified by θ and ϕ , as defined in Figure 6.7.



Figure 6.7. Definition of orientation angles in GSolver®.

For the simulated grating, it was verified that this grating in this orientation only produced a 0R diffractive order in the uncharged state, and only introduced a -1R order when charged. A shallow maximum for -1R diffractive efficiency was found for high θ and ϕ (Figure 6.8). A maximum diffractive efficiency of 1.1×10^{-2} occurred at $\theta = 73^{\circ}$ and $\phi = 83^{\circ}$. This defined the optimal orientation to test the grating.



Figure 6.8. Predicted -1R diffractive efficiency maximum, each contour represent a change of 2×10^{-4} . θ and ϕ defines the orientation in the glass slide superstrate.

With this incident orientation, the incident beam angles and outgoing diffractive angles were also determined. Since this geometrical setup involved two interfaces that were not parallel, Snell's law was applied twice, first at the interface between the glass substrate and the acrylic coupling prism (put into optical contact using type A immersion oil), and again at the interface between the prism and air. Given the three dimensional geometry of the problem, it was necessary to find the plane that contained both the normal of the interface and incident beam before Snell's law could be applied. This was achieved using rotational matrices and coordinate vector geometry. The calculation was carried out in MATLAB. Appendix C contains the m-code used for this calculation. The final solutions were more

conveniently expressed in terms of a spherical coordinate system that aligns to the coupling prism, where the sides of the prism are parallel to the *xz*-plane and the prism face in contact with the sample is parallel to the *xy*-plane (Figure 6.9). Also, to facilitate the alignment of the incident beam, the grating was fabricated at a 7° angle to the edge of the glass slide, such that the incident beam giving the desired $\phi = 83^{\circ}$ had $\theta_{\rm p} = 0^{\circ}$. The predicted directions of the 0R and -1R diffractive orders in the glass slide, in the acrylic prism and in the air are listed in Table 6.1. Note that due to symmetry, the 0R angles also defined the orientation at which the incident beam had to be inserted into the prism to achieve the desired orientation impinging on the grating. In summary, in air, the 0R and -1R diffractive orders would be in a plane roughly parallel with the glass slide, 19° apart from each other, which was a significant deflection angle.



Figure 6.9. Definition of the angles used to describe the outgoing beam directions.

Beam	Glass Slide		Acrylic Coupling Prism		Air	
	<i>φ</i> _p (°)	$ heta_{p}(\degree)$	<i>φ</i> _p (°)	$ heta_{p}(\degree)$	<i>φ</i> _p (°)	$ heta_{p}(\degree)$
0R	73.0	0.0	76.8	0.0	85.5	0.0
-1R	72.6	13.0	76.3	13.0	85.3	19.0

 Table 6.1.
 Predicted exit beam angles for 0R and -1R diffractive orders.

6.3.3 Predicted Performance with Different Grating Thickness and Period

Using the rectangular grating model, the diffractive efficiency of the -1R order was also predicted for different incident orientations with a series of grating period and thickness combinations, in order to get an idea of how the fabrication technique should be optimized in the future. To compare between gratings with different parameters, the orientation with the highest -1R diffractive efficiency was determined and this maximum efficiency was compared against that of gratings with different periods and thicknesses (Figure 6.10). The diffractive efficiency depended only weakly on the charged grating period. On the other hand, the diffractive efficiency increased with increasing grating thickness, which could be expected since the light would interact with the electrode over a longer distance. Thus, a future direction for optimizing the fabrication process may involve reliably creating gratings with greater thickness.



Figure 6.10. -1R diffractive efficiencies for activated diffraction grating models in their respective optimal orientation as functions of (a) the grating thickness and (b) grating charge period.

7 PROTOTYPE GRATING FABRICATION

The fabrication method for the sub-micron pitch variable diffraction grating prototype needed to be able to preserve the nanoporous structure of the $ZnSb_2O_6$ and to achieve the required feature size. The resolution and aspect ratio requirements of this fabrication process were beyond the capability of conventional photolithography. Also, the nanoporous structure introduced additional complications in applying and removing photoresist. Thus, focused ion beam (FIB) milling was chosen because it is able to achieve extremely high limiting feature size (~ 10 nm³⁰) and sufficient aspect ratio. Additionally, FIB was a direct patterning technique, which was beneficial for prototyping, as it facilitated the adjustment of the pattern. However, to use it effectively, a couple other techniques had to be incorporated. First, a protective chromium layer was applied to help preserve the porosity by conducting heat away from the milled line and by protecting the top of the nanoporous layer from stray ion as the ion beam moved around to make different cuts. Second, a critical point drying technique was used to prevent surface tension from destroying the IDE structure while the sample dried after the wet etch used to remove the chromium layer.

7.1 Focused Ion Beam Milling

Because sputtering occurs when a beam of high energy ion impinges on a surface, FIB systems can be used to locally remove or mill away material. It should be noted that while this method is not ideal for high throughput manufacturing due to its serial nature, it is a very powerful prototyping method, since the milling pattern can be easily changed by software. This section provides a brief background on the FIB milling technique, discusses the specific method used for this study, and the presents the limitation on the uncharged grating period and grating thickness that this method imposed.

Most FIB systems use a gallium (Ga) liquid metal ion source, where Ga flows to a needle tip and ions are extracted by field emission. The Ga ions are then typically accelerated to 30 keV^{31} . The ion beam is focused, shaped, and steered in a column that typically consists of two electrostatic lenses, beam-defining apertures, and deflection plates. As the ion beam hits a solid surface, it transfers a large amount of energy into a small region,

causing sputtering and removal of material. The minimum feature size is determined by the beam width, which is ~ 10 nm in state-of-the-art FIB systems, which more than satisfied the requirements for the sub-micron pitch variable diffraction grating.

This study used a FEI DB 235 system which houses an ion column for FIB milling as well as an electron column for taking SEM images during the milling process. To mill a set of 40 μ m × 100 μ m IDEs onto a 25 mm × 25 mm ZnSb₂O₆ sample, the substrate was first scored by hand with a diamond scribe to divide the substrate almost into two halves, except for a roughly 1 mm gap within which the FIB would pattern the IDEs and lines to electrically separate the two sides (Figure 7.1). To prevent charge buildup on the surface, which could cause beam drift, electrical connections with silver conductive epoxy¹⁹ were made from the corners of the sample to the SEM sample holder attached to the bottom of the glass substrate.



Figure 7.1. FIB milled IDEs within narrow gaps between lines scored by a diamond scribe.

Initially, the ion beam was directly applied to the $ZnSb_2O_6$ layer. However, it was observed that the porosity of the layer was severely compromised (Figure 7.2). Compared to $ZnSb_2O_6$ before FIB milling (Figure 3.5), the surfaces appeared much smoother within the cross-section and on the top surface. On the top surface, the nanopores seemed to have coalesced into larger pores with diameter as large as 10 nm. These were both clear indications that the heat imparted onto the $ZnSb_2O_6$ layer had damaged the porous structure. It was also possible that there might have been stray ions that attacked the top surface as the ion beam was steered from one point on the milling pattern to the next. This last motivated the decision to have the beam cut in a serial pattern, where it would cut each line to the full depth before moving, instead of cutting the entire pattern to a series of intermediate depths and cycling multiple times.



Figure 7.2. ZnSb₂O₆ surface after milling with a 100pA beam. The deep rectangular cut was also made by FIB milling after the initial milling to expose the cross-section.

The need to limit the heating of the $ZnSb_2O_6$ layer also limited the milling line density and the milling time, which in turn imposes constraints on the grating period and thickness. It was clear that an efficient means of conducting heat away from the milling region was required in order to make a functional device.

7.2 Protective Chromium Coating

The above observation that heating from the FIB severely damaged the $ZnSb_2O_6$ layer motivated the use of a protective chromium coating. First, the chromium would serve as a sacrificial layer to protect the nanoporous coating from stray ion damage. More importantly, chromium has a much higher thermal conductivity than the nanoporous material, which would help in quickly drawing heat away from the milled region and preserving the nanoporous structure. As a bonus, chromium also has superior electrical conductivity, which would reduce the effect of beam drift due to charge buildup.

A 50 nm thick chromium layer was deposited onto the $ZnSb_2O_6$ layer by electronbeam evaporation, and was removed with a standard chromium etch solution³². Optical and capacitive measurements with unpatterned electrodes verified that the evaporation and etching steps did not significantly affect the $ZnSb_2O_6$ porous layer.

This protective layer was effective in preserving the porosity of ZnSb₂O₆ around the milled region of a grating with uncharged grating period as small as 667 nm (Figure 7.3). The top of the protective surface remained intact during milling. The cross-section of the milled and unmilled regions seemed sufficiently similar, except for a thin layer immediately next to the milled lines where the layer appears brighter in the image. This was likely due to a small amount of heating and/or material redeposition from the sputtering. At the same time, the protective layer enabled a higher ion current to be used, significantly reducing fabrication time from over 6 hours to 2 hours without causing significant damage to the layer. Gratings with uncharged periods of 600 nm and 500 nm were also attempted, but the thinner fingers were less able to draw heat away and the damaged layer grew to be a significant portion of the grating structure.



 Figure 7.3. Cross-section of milled and unmilled areas of a nominally 1500 nm ZnSb₂O₆ sample protected with 50 nm thick protective chromium layer. The pattern of IDEs with 667 nm uncharged grating period was milled at 300 pA.

Note as well that the sidewalls of the cut were not vertical, since it was less likely that the sputtered material would successfully exit the cut line as the cut depth increased. This also made it difficult to ensure electrical separation of between the fingers in thick gratings. It was found that the FIB could reliably cut past the underlying ITO layer for grating thicknesses up to 800 nm (Figure 7.4). To account for this sidewall profile, a modified model was constructed to predict the performance of this grating. Using the dimensions as measured in the SEM scan, the tapered cut lines of the grating were modeled as eight layers of rectangular grating, each with a wider cut line than the last. This modification was verified to not significantly affect the results.



Figure 7.4. Cross-section of milled and unmilled areas of a nominally 800 nm thick ZnSb₂O₆ sample protected with 50 nm thick protective chromium layer. The pattern of IDEs with 667 nm uncharged grating period was milled at 300 pA.

7.3 Critical Point Drying

While the chromium layer successfully ensured reliable fabrication of the sub-micron pitch variable diffraction grating without damaging the porous layer, it also necessitated a wet etch step to remove the chromium after the FIB step. However, the water remaining after the wet etch destroyed the grating as the water evaporated. As the droplet of water diminished in size due to evaporation, the surface tension of the droplet would pull adjacent fingers together. The forces in this case was strong enough to pull the fingers off the substrate and to render the device inoperative (Figure 7.5).



Figure 7.5. IDEs destroyed by evaporating fluid droplets after chromium wet etch.

The effect of such surface tension is typically controlled in MEMS manufacturing by the use of critical point drying (CPD) techniques. With CPD, the fabricated system is first submerged into a fluid in liquid state which replaces any other liquid touching the device surfaces. Then, the thermodynamic state of the system is pushed beyond the critical point of the fluid to make the fluid "supercritical", such that it can smoothly change from liquid to gas without passing through a liquid-gas phase boundary, and therefore without any phase interfaces that would give rise to droplets with surface tension. In this study, the CPD system³³ used carbon dioxide (CO₂) as the working fluid, suitable for a wide range of sample types due to the modest temperature of its critical point (Appendix D). However, liquid CO₂ and water are not miscible and therefore CO₂ could not completely replace the water that was left from the wet etch. Thus, it was necessary to first replace the water with isopropyl alcohol, which is miscible with both water and CO₂. The CPD successfully preserved the IDE structure after the chromium layer was etched off (Figure 7.6).



Figure 7.6. Fabricated IDEs with protective chromium layer removed, showing the preserved nanoporous structure of the top surface.

Using the above three techniques, a prototype was fabricated according to the proposed design described in Section 6.3 (Figure 7.7). The performance of this prototype is discussed in the next chapter.



Figure 7.7. Fabricated 40 μ m \times 100 μ m prototype variable diffraction grating with thickness of 800 nm and uncharged grating period of 667 nm.

8 DIFFRACTION PATTERN FROM A FABRICATED GRATING

The fabricated variable diffraction grating with a thickness of 800 nm and an uncharged period of 667 nm was tested in reflection in the predicted optimal incident geometry as listed in Table 6.1. The glass slide sample containing both IDEs made up the top of the test cell, while a simple glass slide was used as the bottom to form the sealed compartment for the 1.73×10^{-4} M MB-methanol solution. To focus the 650 nm 3 mW diode laser beam onto the grating, an iris aperture and a 35 mm focal length (FL) lens was used before the beam enters the coupling prism to give a beam diameter at the grating of roughly 200 nm. Also, a linear polarizer was aligned and used to ensure that the incident beam was in the p-polarization, in accordance to the simulated setup of the model. The resulting diffraction pattern was observed on a white screen placed 15 cm away from the exit face of the coupling prism.



(a) unchraged

(b) charged

Figure 8.1. Observed diffraction pattern of a variable diffraction grating (800 nm thick, 667 nm uncharged period, and 2.00 μm charged period) when it is (a) uncharged and (b) charged to 1 V.

When a 0.05 Hz square wave varying between 0 V to 1 V was applied, the -1R order was observed to change with the application of a charge voltage (Figure 8.1). There were
some unexpected spots other than the large 0R beam that were present in both states. It was not clear where these came from, though they could be related to the non-vertical side walls as well as the uncontrolled bottom surfaces of the milled lines. The direction and intensity of the modulated diffractive order are presented below, as well as preliminary results of this grating when used with the high speed drive circuit.

8.1 Observed Beam Directions

The 0R and -1R diffractive orders were expected to almost lie in a plane parallel to the bottom face of the coupling prism about 19.0° apart. This agreed very well with the observation. The angle was determined by measuring the spatial separation between the two diffractive orders after propagating a known distance from the prism. This angle was found to be 19.2° . Therefore, the modulated diffractive order was verified to be the -1R order from a grating with a charged period of $2.00 \,\mu\text{m}$.

8.2 Observation of the Modulation of the -1R Diffractive Order



Figure 8.2. Optical setup used to measure the diffractive efficiency of the -1R diffractive order.

To quantify the modulation of the -1R diffractive order, a 0.6 mm thick aluminum sheet with a 6.3 mm diameter hole was used to block out all the diffracted light except that in the area where the -1R diffractive order was observed. This remaining light was focused into an

integrating sphere with a 45 mm FL lens (Figure 8.2). This measured intensity was converted into diffractive efficiency by normalizing by the TIR reflected intensity measured in the same setup except with the sample replaced by a glass slide exposed to air and with the mask removed. This gave a measure of the intensity of the incoming beam while accounting for the various partial reflections.



Figure 8.3. Observed -1R diffractive efficiency with a 1 V square wave applied voltage.

The response time and the amplitude of the modulation of the diffractive efficiency can be seen in Figure 8.3. As hoped, the close spacing between the IDEs did result in significantly faster response time. After the voltage was applied, the change in the diffractive efficiency reached 90% of the steady state change within 250 ms. The diffractive efficiency itself was observed to be 3.9×10^{-3} when in the charged state and 7.9×10^{-4} when in the uncharged state. This gave a charged state/uncharged state contrast of 5:1. While this contrast was high, this was not as high as that predicted with the model, which would predict the diffractive efficiency to be 0 in the uncharged state. One possible contribution of this extra light was the non-directed scattering off the uncontrolled surfaces at the bottom of the milled lines. Also, the charged state diffractive efficiency was less than the expected value of 1.1×10^{-2} . This difference could be due to a range of reasons whose effects had not been well quantified, including some portion of the incident light not hitting the grating due to insufficient focus, and the loss of porosity within the thin layers on each side of the fingers exposed to heat and material redeposition during FIB milling. To provide a rough order-ofmagnitude estimation, a modified GSolver® model where 50 nm on both sides of each finger were replaced by solid $ZnSb_2O_6$ predicted a decreased -1R diffractive efficiency of 4.4×10^{-3} , much closer to the measured value. It was also observed that the optical response was linear with the applied voltage (Figure 8.4). Overall, the fabricated device worked as planned – the sub-micron pitch variable diffraction grating, when uncharged, produced only a 0R diffractive order, and when charged, it introduced a single diffractive order with good contrast and sub-second response time.



Figure 8.4. Observed -1R diffractive efficiency at different applied voltage levels.

8.3 Variable Diffraction Gratings and the High Speed Drive Circuit

Preliminary results were also obtained using the high speed drive circuit with the variable diffraction grating. Optical response time as low as 2 ms was observed, which was comparable to the ramp up time of the input power supply. However, the grating ceased to function within ten cycles and a visible patch of discoloration appeared on the sample, both clear signs that electrochemical reactions had occurred. This was attributed to the different geometrical arrangement of the IDEs, amplifying the effect of the time-varying capacitance because the charge was expected to concentrates itself around the IDEs first. This might

have created a significant overshoot in the charge built up around the IDEs which could be high enough to drive electrochemical reactions. Based on these observations, it seems that optimization of the high speed drive circuit is necessary in order for it to be a practical solution for long term actuation of a device.

9 CONCLUSION

This study aimed to improve the understanding of the behavior of electrophoretic ionic optical devices and to explore their potential for use in practical devices. Specifically, the sub-micron pitch variable diffraction grating was evaluated for its potential for non-mechanical beam steering applications. For improving the practicality of electrophoretic ionic optical devices, an electron tunneling model of the electrochemical threshold was developed and verified. For implementation of a sub-micron pitch variable diffraction grating, the electrical and optical behavior of MB ionic dye within nanoporous ZnSb₂O₆ conductive thin film were measured, and a prototype sub-micron pitch variable diffraction grating was fabricated to demonstrate the modulation of the diffractive efficiency at good contrast and sub-second response time.

One of the remaining major hurdles for electrophoretic ionic optical devices for use in practical applications has been the onset of undesirable irreversible electrochemical reactions at high applied voltages, which in turn limits the response time. To better optimize the response time and the device lifetime, an electron tunneling model for the electrochemical threshold was developed and verified. This model predicted that, in transient situations during charging and discharging, the accumulated charge within the electric double layer around each electrode is a better predictor of electrochemical reaction than the voltage applied across the two electrodes. Therefore, it is possible to apply a high voltage for a very short time to induce quick ion movement and optical response without inducing electrochemical reactions. Using a high speed drive circuit constructed with capacitors and resistors, the response time of a test system was reduced from 5 s to 0.1 s. After 8 hours of cycling using the high speed drive circuit, the test systems showed comparable long term behavior as cases where low amplitude square wave voltages were used, demonstrating that the response time vastly improved without compromising the device lifetime. The development of the electron tunneling model had enabled significant optimization in the response time and lifetime of electrophoretic ionic optical devices.

A better understanding of the electrical and optical properties of the MB-methanol electrolyte around the ZnSb₂O₆ nanoporous electrodes was also needed in order to better

model and optimize the behavior of the variable diffraction grating. Due to its nanoporous structure, it was observed that the charging curve of ZnSb₂O₆ nanoporous electrodes in MBmethanol electrolyte had a time-varying capacitance, since the dye ions was expected to require a certain amount of time to reach electrode surface deep within the pores. The steady state electrochemical threshold voltage was measured to be 1.2 V for this electrodeelectrolyte pair. Also, it was found that in the uncharged state, the concentration of the dye ions within the pores of the electrodes was higher than that in the bulk electrolyte. This was attributed to the increased surface area of the nanoporous electrode whereby much of the pore volume regions in the electrode was within a monolayer of the surface. Both types of ions could tend to have higher concentration within this monolayer. Thus, as a voltage bias was applied across the two electrodes, optical changes could occur by charging the electrode with dye ions or by forcing out of the electrode the initial dye ions present. Thus, the fractional difference in absorption properties between the two electrodes for a MB-methanol electrolyte could be maximized by completely depleting one of the electrodes of dye ions. This was observed to occur for an applied voltage magnitude of 1 V at a bulk concentration of 1.73×10⁻⁴ M. Furthermore, it was observed that the optical changes could only account for less than 6% of the total accumulated charge on the electrodes, indicating that the smaller transparent counter-ion moved significantly faster than the MB dye ions. The complex refractive indices of the layer when charged to +1 V and -1 V were directly measured for use in the model of the prototype grating.

A simple prototype for the variable diffraction grating in the form of two IDEs was designed and constructed. This setup allowed switching between two grating periods. The geometry of the IDEs had a significantly smaller separation between the electrodes, enabling a faster response time. The dimensions of the prototype grating design were determined by efficiency considerations and fabrication limitations. For the prototype, it was decided that every third finger would be darkened to achieve a higher efficiency while maintaining a high deflection angle. The thickness of the grating was set to 800 nm and the uncharged grating period to 667 nm, due to limitations of the fabrication method. Though modeling predicted that higher efficiencies could be reached with larger grating thickness, the chosen fabrication technique could not readily achieve grating thickness beyond 800 nm. In the optimal

orientation, the grating was predicted to have a -1R diffractive efficiency of 1.1×10^{-2} , which should exit the setup in air 19.0° from the 0R diffractive order.

A prototype grating conforming to the above design was successfully fabricated using a FIB milling technique. A protective chromium layer was necessary to preserve the nanoporous structure of the $ZnSb_2O_6$. Also, CPD was used to ensure that the IDEs remained intact after the wet etch that was used to remove the chromium layer.

When tested, the fabricated prototype was observed to be able to modulate the diffractive efficiency of the -1R diffractive order. The exit geometry agreed very well with the prediction. After the voltage was applied, the diffractive efficiency change reached 90% of the maximum in 250 ms. The diffractive efficiency itself was observed to be 3.9×10^{-3} when in the charged state and 7.9×10^{-4} when in the uncharged state. This gave a charged state/uncharged state contrast of 5:1. While the charged state diffractive efficiency was less than the expected value of 1.1×10^{-2} , this difference could be attributed to a combination of reasons, including some light not hitting the grating due to insufficient focus, and the loss of porosity within the thin layers on the sides of each finger exposed to heat and material redeposition during FIB milling. While preliminary results suggested that the high speed drive circuit could also greatly improve the response time of the variable diffraction grating, a more complicated circuit seemed to be required to better account for the time-varying capacitance of the nanoporous IDEs. Overall, the prototype sub-micron pitch variable diffraction grating demonstrated that, as planned, this type of device, when uncharged, would produce just the 0R diffractive order and, when charged, would introduce a single new diffractive order with sub-second response time and high deflection angle.

Thus, this study established that this type of device continues to show promise for further development for non-mechanical beam steering applications, and suggests a number of future directions for experimentation.

This study verified that the high speed drive circuit was very effective in reducing the response time of these devices. However, due to the time-varying capacitance of the nanoporous electrodes, a more complicated circuit must be designed to produce a smoother response curve to maximize the effectiveness of the circuit.

Furthermore, it is desirable to further increase the -1R diffractive efficiency of the device in its charged state. One way would be to increase the fraction of the total accumulated ionic charge in the electrodes that is due to the dye ion instead of the counterion. Thus, it may be beneficial to experiment with ionic dyes that have a larger counter-ion, or porous conductor with larger pores. These have the potential to vastly increase the optical change within the electrode for a given applied voltage, thus greatly increase the -1R diffractive efficiency of the charged grating.

Also, modeling predicted that a thicker grating would have a higher -1R diffractive efficiency. To fully exploit this, further experimentation with the FIB technique to reliably mill deep grooves through a thicker nanoporous layer must be performed.

Another standard way to raise the diffractive efficiency for a particular diffractive order is to move beyond simple rectangular gratings and use blazed grating designs. In a blazed grating, the reflective surfaces of the grating are at an angle with the direction in which the refractive index of the grating modulates. A blazed variable diffraction grating may be achievable by first employing standard technique to make a blazed grating before separating the individual lines into IDEs using FIB techniques.

REFERENCES

- L. Eldada, "Advances in telecom and datacom optical components," *Opt. Eng.* 40, 1165-1178 (2001).
- 2. J. F. Heanue, M. C. Bashaw, and L. Hesselink, "Volume holographic storage and retrieval of digital data," *Science* **265**, 749-752 (1994).
- 3. X. Liu, D. Du, and G. Mourou, "Laser ablation and micromachining with ultrashort laser pulses," *IEEE J. Quantum Electron.* **33**, 1706-1716 (1997).
- P. F. McManamon, T. A. Dorschner, D. L. Corkum, L. J. Friedman, D. S. Hobbs, M. Holz, S. Liberman, H. Q. Nguyen, D. P. Resler, R. C. Sharp, and E. A. Watson, "Optical Phased Array Technology," *Proc. of the IEEE* 84, 268-298 (1996).
- M. Flood and B. Gutelius, "Commercial Implication of Topographic Terrain Mapping Using Scanning Airborne Laser Radar," *Photogrammetric Engineering & Remote Sensing* (April 1997), 327-329, 363-366 (1997).
- 6. J. M. Younse, "Mirrors on a chip", IEEE Spectrum (1993).
- J. Kim, C. Oh, M. J. Escuti, L. Hosting, and S. Serati, "Wide-angle, nonmechanical beam steering using thin liquid crystal polarization gratings," *Proceedings of SPIE* 7093, 709302 (2008).
- P. C. P. Hrudey, M. A. Martinuk, M. A. Mossman, A. C. van Popta, M. J. Brett, J. S. Huizinga, and L. A. Whitehead, "Variable diffraction gratings using nanoporous electrodes and electrophoresis of dye ions," *Proc. SPIE* 6645, 66450K (2007).
- P. Hrudey, M. Martinuk, M. Mossman, A. van Popta, M. Brett, T. Dunbar, J. Huizinga, and L. Whitehead, "Application of transparent nanostructured electrodes for modulation of TIR", *Proc. of SPIE* 6647, 66470 A, 1-12. (2007).

- R. T. F. Wong, P. C. P. Hrudey, and L. A. Whitehead, "Electrochemical threshold conditions during electro-optical switching of ionic electrophoretic optical devices," Appl. Opt. 48, 1062-1072 (2009).
- 11. E. Hecht, *Optics*, 4th ed. (Addison Wesley, 2002).
- J. Sancho-Parramon and V. Janicki, "Effective medium theories for composite optical materials in spectral ranges of weak absorption: the case of Nb₂O₅-SiO₂ mixtures," *J. Phys. D: Appl. Phys.* 41, 215304 (2008).
- 13. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications, 2nd ed.* (John Wiley and Sons, 2001).
- 14. H. Ohshima, "Electrokinetic Behavior of Particles: Theory," *Encyclopedia of Surface and Colloid Science*, 302-322 (CRC Press, 2004).
- 15. G. S. Singhal and E. Rabinowitch, "Changes in the absorption spectrum of methylene blue with pH," *J. Phys. Chem.* **71**, 3347-3349 (1967).
- K. L. Kostka, M. D. Radcliffe, and E. von Meerwall, "Diffusion Coefficients of Methylene Blue and Thioflavin T Dyes in Methanol Solution," *J. Phys. Chem.* 96, 2289-2292 (1992).
- 17. Nissan chemical industries CELNAX CX-Z330H-F2.
- 18. Delta Technologies product no. CG-90IN-S115.
- 19. MG Chemicals Silver Conductive Epoxy, Cat. No. 8331.
- K. B. Oldham and J. C. Myland, *Fundamentals of Electrochemical Science* (Academic Press, 1994).
- R. W. Gurney, "Theory of electrical double layers in adsorbed films," *Phys. Rev.* 47, 479-482 (1935).

- R. A. Marcus, "Electron transfer reactions in chemistry. Theory and experiment", *Rev. Mod. Phys.* 65(2), 599-610 (1993).
- B. H. Bransden and C. J. Joachain, *Quantum Mechanics*, 2nd ed. (Pearson Education, 2000).
- 24. R. J. White and H. S. White, "Electrochemistry in nanometer-wide electrochemical cells", *Langmuir* 24, 2850-2855 (2008).
- 25. HP 33120A Function Generator/Arbitrary Waveform Generator.
- 26. Melles Griot Large Dynamic Range Amplifier.
- Y. Wang, W. P. Chen, K. C. Cheng, H. L. W. Chan, and C. L. Choy "Effect of AC-powered water electrolysis on the structural and optical properties of indium tin oxide thin films", *J. Am. Ceram. Soc.*, 88 [4] 1007–1009 (2005).
- 28. National Instrument NI 6013 Data Acquisition Card.
- 29. Kepco BOP 200-1M Bipolar Power Supply.
- C. A. Volkert and A. M. Minor, "Focused Ion Beam Microscopy and Micromachining," MRS Bulletin 32, 389-399 (2007).
- W. J. MoberlyChan, D. P. Adams, M. J. Aziz, G. Hobler, and T. Schenkel, "Fundamentals of Focused Ion Beam Nanostructural Processing: Below, At and Above the Surface," *MRS Bulletin* 32, 424-432 (2007).
- 32. Transene Cr-1020AC.
- 33. Tousimis Autosamdri®-815B Critical Point Drying System.

APPENDIX A: GSOLVER® DIFFRACTION GRATING SIMULATION SOFTWARE PACKAGE

The GSolver® software package implements the rigorous coupled-wave analysis technique to determine the diffractive efficiencies of diffractive orders from gratings whose index modulation can occur in up to three dimensions. The analysis technique solves Maxwell's equations exactly for a truncated Fourier expansion of the permittivity of the grating layer. Arbitrary accuracy can be reached depending on how many Fourier terms are kept for the analysis. This appendix qualitatively outlines the flow of the setup and solution of the analysis, and also discusses how to precisely define a grating model in GSolver® using text files as input. This study used version 5.1 of this program. Full details of the analysis can be found in the user manual^{*}.

First, the grating features are approximated to be a piecewise constant, periodic, and lamellar structure, though this can be done to the desire level of detail to accurately approximate arbitrarily complex grating structures. The grating is at the boundary between semi-infinite superstrate and substrate regions. The superstrate is defined to be transparent, so that a unity-amplitude plane wave can be defined to be impinging on the grating from the superstrate. The plane wave's orientation is defined by two polar angles, and its polarization state can be elliptical in general and is defined by two polarization angles.

The periodic changes in refractive index in the grating region are similarly reflected in the permittivity. Thus, the permittivity can be expressed as a Fourier expansion. Using this expansion and periodic boundary conditions (in the transverse directions), Maxwell's equations that relate the transverse electric field and transverse magnetic field can be cast into a coupled differential equation, which can be solved using an Algebraic Eigensystem method. This would lead to solutions of the field equations with a number of amplitude coefficients. Then, the boundary conditions for tangential components for the electric and magnetic fields are used to determine these coefficients. Thus, fields internal to each lamella of the grating can be found. The reflective and transmissive diffractive orders exiting the grating are computed by solving fields at top and bottom interfaces. This method can therefore analyze grating structure of high complexity to an desired accuracy. An inherent convergence test can be performed by comparing the results while including an increasing number of Fourier components of the permittivity in the analysis.

¥	2_0ur	m per	iod 1	V.gs5	- GSo	lver¥5	1								
Eile Edit Format Formulas View Iools Grid Component About															
D ☞ 🖬 ¾ 🖻 📾 🛥 🦷 🗠 ¼															
Parameters Editor Listing/RUN GA Run Results 3D Editor 3D Run Angles Calc															
2D Editor Grating Editor vertical scale factor: 1															
	0	1	²	3	4	⁵ ا	i	6	7	8	9	10	11	12	
4 5 6 7 7 8 9															
¹ ² ³															
<u> </u>											 	5:00	D PM	NUM	AE /

Figure A.1 GSolver® interface and graphical representation of a typical rectangular grating used to simulate the fabricated IDEs.

The software package features an intuitive graphical interface to specify the model parameters, as well as to display the results. The geometrical features of the grating can be specified in multiple ways, the most precise of which is to use an input text file via the "Text Import" command, where the fractional width (in units of one grating period) of each area of constant refractive index within each layer can be precisely specified. The width in each of the layers must add up to unity.

For example, the rectangular grating model used to simulate the fabricated grating (Figure A.1) was specified by a text file with the following text input:

[LAYER	2]		
.8			
0.10	CONSTANT	MB.in.MeOH	false
0.23333	CONSTANT	ZnSBOinMB.MeOH.m1V	false
0.10	CONSTANT	MB.in.MeOH	false
0.23333	CONSTANT	ZnSBOinMB.MeOH.m1V	false
0.10	CONSTANT	MB.in.MeOH	false
0.23334	CONSTANT	ZnSBOinMB.MeOH.1V	false
[LAYER	2]		
0.020			
0.10	CONSTANT	MB.in.MeOH	false
0.23333	CONSTANT	ITO2	false
0.10	CONSTANT	MB.in.MeOH	false
0.23333	CONSTANT	ITO2	false
0.10	CONSTANT	MB.in.MeOH	false
0.23334	CONSTANT	ITO2	false
[END]			

In this text file, "[LAYER]" defines a new layer, successively built from the substrate up. The number below that defines the thickness of the layer in microns. Each subsequent line defines, respectively, the fractional width of a particular rectangular grating feature, the refractive index model type, the refractive index model name for the desired material, and whether the refractive index varies with the wavelength of the light.

The refractive index models can be user-specified in the setup file "Gsolver.ini" found in the same folder as the program executable. Since this study focused on behavior of the grating with light within a narrow band around 650 nm, constant models were used with the values as listed in Table 5.1. In this case, the corresponding entries in "Gsolver.ini" to specify the above models are as follows:

[CONSTANTS] total = 6 Glass: 1.517, 0 ITO2: 1.775, 0.012 MB.in.MeOH: 1.329, 0.00019 ZnSBOinMB.MeOH.1V: 1.570, 0.014 ZnSBOinMB.MeOH.m1V: 1.570, 0.0035 Using these two sets of input, the simulations done during the course of this study can be reproduced.

^{*} D. Fluckiger, *GSolver V5.1 Users' Guide*, <u>http://www.gsolver.com/UserManual.pdf</u> (accessed 2009 July 09), 2009.

APPENDIX B: SAMPLE PREPARATION PROCEDURES FOR NANOPOROUS ZINC ANTIMONATE THIN FILMS

This is the procedure used to prepare all transparent nanoporous zinc antimonate $(ZnSb_2O_6)$ samples for this study. To achieve a desired thickness, the viscosity of the $ZnSb_2O_6$ dispersion was adjusted using polyethylene glycol before this dispersion was spin-coated onto the sample substrate at an appropriate spin speed.^{**}

Required Equipment:

- Indium tin oxide (ITO)-coated glass
- Isopropyl alcohol (IPA) a.k.a. 2-propanol
- Acetone
- Dry N₂
- Various beakers
- Celnax CX-Z330H ZnSb₂O₆ dispersions (CX-Z330H-F2 has 15 nm primary particle size, and CX-Z330H has 20 nm primary particle size).
- Polyethylene glycol (PEG)
- Triton X-100
- Hot plate
- Spinner
- Vacuum pump (exhausted to exterior of building)
- Spinner chuck
- Aluminum foil
- Ethanol squirt bottles
- Kim wipes
- Wafer tweezers
- Diamond scribe
- Square-sided small polystyrene weigh boats
- Multimeter
- Pipettes
- Pipette bulbs

Dispersion Preparation Procedure:

- 1. Weigh out desired amount of Celnax material.
- 2. Add deionized water (if diluting Celnax material).
- 3. Add desired mass of Triton X-100.
- 4. Add desired mass of PEG.
- 5. Put spinner bar in container, close lid, and stir on stirrer plate for 2+ hours (stir at setting 4 or lower).
- 6. Periodically stir with stir stick to ensure dissolution of PEG.

(note: a typical recipe is 64:1:1 mass ratio for Celnax:Triton X-100:PEG)

Electrode Preparation Procedure:

- 1. Use diamond scribe to cleave ITO-coated glass into desired sample sizes and to label samples appropriately.
- 2. Immerse ITO-coated glass samples in beaker filled with acetone.
- 3. Suspend beaker of acetone in ultrasonic bath (filled with distilled water).
- 4. Run ultrasonic bath for 2 cycles (~ 10 minutes total).
- 5. Move samples to beaker of IPA, and suspend beaker in ultrasonic bath.
- 6. Run ultrasonic bath for 2 cycles (~ 10 minutes total).
- 7. Place hot plate in a safe location (flow hood or fume hood without any flammable materials nearby).
- 8. Turn on hot plate to setting 8.5 (~ 450 °C) and let heat up for 15 20 minutes.
- 9. Line spinner basin with aluminum foil.
- 10. Turn on spinner.
- 11. Turn on vacuum pump.
- 12. Open vacuum valve on spinner (press "vacuum" button).
- 13. Take one sample out of IPA, and blow dry with N_2 gas.
- 14. Use multimeter to confirm which side of ITO-coated glass is conductive.
- 15. Mount sample onto spinner chuck with conductive side up. (If desired, cut out bottom of weigh boat and placed on spinner chuck first and punch a hole in center of it helps to improve thickness uniformity of samples).
- 16. Check to ensure that sample is solidly held onto chuck by vacuum.
- 17. Place lid on spinner.
- 18. Perform test spin to ensure that sample stays in place on chuck, and to tune the speed settings to the desired speed.
- 19. Use pipette to aspire some of ZnSb₂O₆ dispersion and then dispense onto surface of sample so that entire surface is covered in fluid.
- 20. Place lid on spinner.
- 21. Spin sample. (note: typically 3000 rpm for 45 seconds with no pre-spinning)
- 22. Once spinning is complete, remove sample from chuck.
- 23. Use acetone-soaked Kimwipe to remove any ZnSb₂O₆ material on backside of sample.
- 24. Use N_2 gas to ensure acetone completely evaporates from backside of sample.
- 25. Place sample onto hot plate leave on hot plate for at least 30 minutes. (NOTE: if some acetone is still evaporating from sample or if some air is trapped under the slide due to fast dropping towards the hotplate, sample may crack in two when placed on hot plate).
- 26. Spin all other samples similarly.
- 27. After all samples have been baked for 30 minutes, turn hot plate off. Remove samples to thermally conductive surface, if desired.

^{**} Adapted from procedures composed by P. C. P. Hrudey, 2008.

APPENDIX C: MATLAB M-CODE USED TO PREDICT THE OUTGOING BEAM DIRECTIONS

Since GSolver® only predicts the outgoing diffraction angles in the glass slide superstrate, the following MATLAB m-code performs two Snell's law calculations to determine the propagation angles in the acrylic coupling prism and then in air. Due to the geometrical setup of the problem, it was necessary to perform a number of co-ordinate transformations.

%calculates refraction of an incident angle at an interface in 3D space, %defined by 2 angles

n2 = 1.; %input material n1 = 1.49; %output material

%angle defined wrt normal of bottom of prism %(xy plane is bottom of prism, normal to prism face is in xz plane) thetal =-12.97; %function input phi1 = 76.322; %function input theta = (thetal)/180*pi; %rad phi = (phi1)/180*pi; %rad

%define unit normal to prism face n = [sin(60/180*pi); 0; cos(60/180*pi)]; %function input

%vector of incoming light l = [sin(phi)*cos(theta); sin(phi)*sin(theta); cos(phi)];

```
%normal to plane containing both vectors
p = cross(n, l)/norm(cross(n,l));
phip = acos(p(3)/norm(p));
thetap = acos(p(1)/norm(p)/sin(phip));
```

```
%get angle between n and l
alpha = acos(dot(n,l));
```

%snell's law beta = asin(n1/n2*sin(alpha))

%we know exit vector, is n rotated by beta around p %so use rotation transform to rotate coordinate system

```
Rcoord1 = [cos(-thetap), -sin(-thetap), 0; sin(-thetap), cos(-thetap), 0; 0,0,1];

Rcoord2 = [cos(-phip), 0, sin(-phip); 0,1,0; -sin(-phip), 0, cos(-phip)];

Rcoord2 = Rcoord2*Rcoord1;
```

 $Rbeta = [\cos(beta), -\sin(beta), 0; \sin(beta), \cos(beta), 0; 0,0,1];$

Rcoordneg = inv(Rcoord);

exit = Rcoordneg*Rbeta*Rcoord*n;

thetaout = atan(exit(2)/exit(1))*180/pi %output in degrees phiout = acos(exit(3)/norm(exit))*180/pi %output in degrees

```
%visualizing vectors
zero = [0,0,0];
arrow3d([-1,0, 0; -n'; -l'; zero; zero], [1, 0, 0;n'/2; zero; p'; exit'])
axis equal; grid on;
hold off
```

APPENDIX D: CRITICAL POINT DRYING

As a liquid evaporates off of a surface, the shrinking liquid droplets can damage the surface because of surface tension. This problem of surface tension is especially pronounced around of microstructures where the vanishing droplets can pull different parts of the structure together. In the field of microelectromechaical systems (MEMS), this is a common cause of catastrophic failure of the fabricated devices^{***}. A similar problem was encountered in this project during the fabrication of the interdigitated electrodes.



Figure D.1. Different methods of drying represented by different paths for state transition from a liquid state A to a gas state B.

The effect of such surface tension is typically controlled in MEMS manufacturing by the use of critical point drying (CPD). With conventional drying techniques, for example, by blowing with dry nitrogen gas or by heating the surface, the liquid is turned into gas through crossing the liquid-gas phase boundary, wherein both gas and liquid exist for a period time and forms pockets of different phases. This creates interfaces between phases which give rise to surface tension. By controlling the pressure and temperature of the fluid system, CPD moves the system beyond the critical point of the fluid, and around the liquid-gas phase boundary (Figure D.1). Therefore, the fluid transitions from a liquid state to a gas state without interfaces around droplets of different phases, avoiding the adverse effect of surface tension.

Typically, the working fluid in CPD systems is carbon dioxide (CO₂), which was also used in the Tousimis Autosamdri®-815B system used for this study. CO₂ offers a number of advantages, including being non-hazardous, virtually inert, ozone friendly, and readily available, while having relatively low critical pressure and critical temperature at 31.1 °C and 73 atm, respectively.

Liquid CO_2 , however, is not miscible with water, so it has limited ability to replace all the water out of the microstructured surface. Therefore, to dry a sample that have been exposed to water, the water is typically first replaced by ethanol or isopropyl alcohol before CPD is performed.

The CPD cycle involves a few simple steps. To start the transition where CO_2 is in the liquid state, the test chamber containing the sample and the alcohol would be cooled down. Then, liquid CO_2 would be injected into the test chamber to replace the alcohol. This would repeat in a number of filling and purging cycles to ensure that the CO_2 has completely replaced the alcohol and is the only fluid in contact with the sample surface. At that point, the CPD transitions take place while the pressure and temperature is controlled by the CPD system. At the end of the cycle, the sample would be fully dried without any damage from surface tension of liquid-gas interfaces.

^{***}I. Jafri, H. Busta, and S. Walsh, "Critical Point Drying and Cleaning for MEMS Technology," *Proc. SPIE.* **3880**, 51 (1999).