ABSTRACT

Title of Dissertation:	NOVEL AQUEOUS-BASED
	ELECTROLYTES AND ELECTRODE
	SYSTEMS FOR THE NEXT GENERATION
	OF AQUEOUS LITHIUM-ION BATTERIES
	Nicolas Thierry Eidson, Doctor of Philosophy,
	2022

Dissertation directed by:

Professor Chunsheng Wang, Department of Chemical and Biomolecular Engineering

Aqueous Li-ion batteries are a vital component for the future electrification of society. Their extreme safety and reduced manufacturing costs could enable them to fit into many niche markets. Current aqueous Li-ion battery systems suffer from many of the same form factor restrictions as organic Li-ion batteries and rely heavily on maximizing the amount of LiTFSI in the system at the cost of important properties such as electrolyte cost, viscosity, and ionic conductivity in order to maintain the highly concentrated electrolyte classification. They are also limited by the lack of suitable anodes to replace the dominant choice of LTO. Much of the advancement in recent years has been due to the focus on improving the SEI with less attention paid to other important concerns. The goal of this research is not only to continue advancing the limits of aqueous Li-ion batteries, but to shed light on some of the other areas that are often overlooked but of equal importance. Reported here are three key advancements in the development of a novel aqueous cell chemistry for form factor, electrolyte, and anode. First is the development of a gel polymer electrolyte and gel protection layer for the fabrication of a flexible 4V aqueous Li-ion battery employing a Graphite/LCO electrode pair, with focus given to the system's feasibility to be transitioned to industry. Second, the development of a safer hybrid electrolyte and subsequent transition from the highly concentrated electrolyte regime to the first reported localized highly concentrated hybrid aqueous/non-aqueous electrolyte. Finally, the first incorporation of TNO as an anode replacement for LTO. With the combination of this novel electrolyte and aqueous anode chemistry, a TNO/LMO full cell using a 1,4-dioxane diluted water/TEP co-solvent electrolyte provided an initial discharge capacity of 187 mAh/g reaching a Coulombic efficiency of >99.5% and a capacity retention of 92% after 90 cycles at a cycling cutoff potential of 2.8V.

NOVEL AQUEOUS-BASED ELECTROLYTES AND ELECTRODE SYSTEMS FOR THE NEXT GENERATION OF AQUEOUS LITHIUM-ION BATTERIES

by

Nicolas Thierry Eidson

Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctor of Philosophy 2022

Advisory Committee: Professor Chunsheng Wang, Chair Associate Professor Yifei Mo, Dean's Representative Assistant Professor Paul Albertus Professor Dongxia Liu Associate Professor Taylor J. Woehl Dr. Kang Xu © Copyright by Nicolas Thierry Eidson 2022

Dedication

Dedicated to my loving wife, Romy. Without your support and encouragement, this would not have been possible. I love you.

Acknowledgments

First and foremost, I wish to thank the support from my advisor, Professor Chunsheng Wang. His mentorship has balanced between providing me with support and guidance when I need it and with belief and space to pursue my intellectual endeavors. He has a way of being able to always have an answer to all my most puzzling problems as if they are stored away in a magical pocket.

I would also like to thank the tremendous support I received from everyone I worked alongside at the US Army Research Laboratory. A big thank you to Drs. David R. Baker, Oleg Borodin, Jonathan Boltersdorf, Janet Ho, Marshall Schroeder, Jan Allen, Dat Tran, Michael Ding, Jeff Read, Yakira Howard, Harold Sun, Kang Xu, Arthur Cresce, and anyone else I may have inadvertently left off. Whether it was showing me how to use some equipment, providing me with experimental suggestions, or some general advice, it was a pleasure and a joy to work with all of you. I especially want to thank my supervisor, Dr. Xu, for not only providing me with this amazing opportunity, but also for providing me with the scientific knowledge that only a true field expert could provide. And finally, I would like to give a tremendous thank you to Dr. Cresce. For the past 6+ years, he has been my mentor and colleague nearly every step of the way. In the beginning, he was the man with a million ideas and endless energy. Then he became the man with a million ideas, no energy, and two wonderful twin boys. And in the end, he returned to the man with a million ideas and endless energy, but a curfew to head home to take care of the boys. It was a joy commuting the hour and a half to APG when our facilities were down for weeks and

talking about anything as we drove. He has been a true asset in my academic growth, and he has been a true companion during my time at ARL.

Another special thanks to everyone in my lab at the University of Maryland and my professors and classmates at UMD. I want to especially thank Drs. Fudong Han, Jie Yue, Fei Wang, Chongyin Yang, Chao Luo, Singyuk Hou, and Tao Gao. You all have dramatically increased my knowledge and given me a community of support. I would also like to thank Dr. Peter Kofinas for his in-depth knowledge in the field of polymers and his generous offer to utilize his laboratory space when my normal lab space was down. And as anyone knows, a Ph.D. is a stressful endeavor that is only possible thanks to the tremendous social network your classmates provide. A big thank you to Dr. James Corson and Louie Coplan for the help in all our courses. I wouldn't have passed without you two. Thanks to the friendship from Drs. Mei Wang, Dennis Tran, Emily Schulman, Derrick Ko, and the soon-to-be Drs. Xinzi He and Kyle Ludwig, and everyone else that made my time at UMD special.

Last but not least, I want to thank my family. My father, Dr. Thomas Eidson, has been a constant source of support and advice in both my engineering courses and my research. My mother, Louise Edwards, and my siblings, Christine Daniels and Max Edwards, have provided me with love and support through these challenging years. Thank you to the rest of my extended family, whether in the US, Canada, or China, having you in my life has made these challenges bearable. And of course, I couldn't leave off the comfort provided by my amazing dogs, Goldie "Gougou" and Houdini. Finally, thanks to the other Ph.D. in the house, Dr. Romy Ren Wang. I finally caught up to you thanks to your endless motivation and love.

iv

Table of Contents

Dedication	ii
Acknowledgments	. iii
Table of Contents	v
List of Tables	vii
List of Figures	viii
List of Abbreviations	viii
Chapter 1: Introduction	1
1.1 Lithium-Ion Batteries	1
1.1.1 Market Demand	1
1.1.2 Current State-of-the-Art LIBs	1
1.1.3 Alternative Secondary Batteries	2
1.2 Aqueous Lithium-Ion Batteries	4
1.2.1 Birth of the ALIB	4
1.2.2 Electrolyte Breakthroughs	6
1.2.3 Aqueous Electrolyte Limitations	10
Chapter 2: Aqueous Gel Polymer Electrolytes	14
2.1 3V Gel Batteries	14
2.1.1 Introduction	14
2.1.2 Gel Polymer Electrolyte Development	15
2.1.3 Gel Polymer Electrolyte Properties	19
2.2 4V Gel Batteries	26
2.2.1 Introduction	26
2.2.2 Gel Protection Layer	27
2.2.3 Full Cell: Materials and Methods	29
2.2.4 Full Cell: Results and Discussion	33
Chapter 3: Electrolyte Modification	39
3.1 Hybrid Aqueous/Non-Aqueous Electrolyte	39
3.1.1 Introduction	39
3.1.2 Organic Phase Replacement	40
3.1.3 TEP Hybrid Electrolyte Results and Discussion	41
3.2 Electrolyte Diluent	51
3.2.1 Introduction	51
3.2.2 Fluorinated Ether Diluent	52
3.2.3 1,4-Dioxane Diluent	59
Chapter 4: Anode Modifications	77
4.1 Anode Chemistry	77
4.1.1 LTO	77
4.1.2 TNO	79
4.1.3 PNO (Titanium Free)	82
4.2 Anode Coatings	85
4.2.1 Grafting.	85
4.2.2 Electrode Particle Coatings (Carbon, LATP, LiF)	88
Chapter 5: Summary and Future Directions	97

5.1 Project Summaries	
5.1.1 Gel Polymer Electrolyte	
5.1.2 Electrolyte Modification	
5.1.3 Anode Modifications	
5.2 Future Directions for Aqueous Lithium-Ion Batteries	
5.2.1 Protecting the Anode	
5.2.2 Stabilizing the Electrolyte	100
5.2.3 Alternative Electrode Chemistries	101
5.2.4 Cheaper/Safer Alternatives	101
5.2.5 Concluding Remarks	
Bibliography	105
Publications and Presentations	

List of Tables

Table 1: Molar composition of HTe-21 + fluorinated ether diluent electrolytes....... 53Table 2: Molar compositions of tested HDTe-2X1 electrolytes compared to the HDO-12 system showing which molar rations were held constant in red....... 61

List of Figures

Figure 1: (A) Relative strengths and weaknesses of various battery technologies including LIB, Na- and K-ion batteries (NIB and KIB), all-solid-state batteries, and multivalent batteries. (B) Calculations of various battery active materials using the BatPaC model. Reprinted with permission from Figure 3: (A) Reductive and (B) oxidative potential magnifications of (C) the electrochemical stability window for various aqueous LiTFSI electrolytes. Reprinted with permission from [10]. Reprinted with permission from AAAS......7 Figure 4: (A) Extended electrochemical stability window of the HANE electrolyte. (B) Cyclic voltammogram showing additional SEI formation process in early cycles. (C) Schematic of SEI formation from both salt and organic Figure 5: (A) Schematic of dilution effect in LHCE. (B) Flammability test of glass fiber soaked separators. (C) Viscosity comparison of base highly concentrated electrolyte, LHCEs, and standard organic electrolyte. Figure 6: Discharge capacities and Coulombic efficiencies (CE) of LTO/LMO full cells. Reproduced with permission from [20]. Copyright 2021 American

Figure 7:	(A) 4V stability window of electrolyte. (B) Stabilization of graphite
	lithiation with the aqueous electrolyte. The voltage profile (C & E) and
	cycling stability (D & F) of LiVPO ₄ F vs. Li metal and graphite,
	respectively, at a rate of 0.3C. The capacity is based on the cathode mass.
	Reproduced with permission from [13]15
Figure 8:	(A) Structures acrylate monomers (MPEGA480 and HEA), diacrylate
	crosslinker (PEGDA700), and photoinitiator (DMPA). (B) Schematic of
	crosslinked gel electrolyte showing both intra- and interchain
	crosslinking. The electrolyte would occupy the white space. Modified
	from [23]
Figure 9:	(A) ESW of the base WIBS, W-GPE, and C-W-GPE. (B) Ionic conductivity
	of three different monomer formulations for W-GPE and C-W-GPE.
	Reproduced with permission from [22]. Copyright Royal Society of
	Chemistry 2019 19
Figure 10): Photo of thermoconductometric cell with polypropylene bottle, nickel
	electrodes, and sample solution prior to UV radiation. Use of
	polypropylene bottle was ideal as it is UV transparent and can cut after
	curing to remove electrodes without damaging them. Reproduced with
	permission from [24]
Figure 11	1: TCA curves of differential temperature (a) and conductivity (b) versus
	temperature for the pre- and post-UV samples with (A) w=0.060, (B)
	w=0.120, and (C) $w=0.230$. The baseline electrolyte ($w=0$) is plotted for

Figure 19: TGA analysis of the GPE (black) and GPL (red)......35

Figure 20: Ionic conductivity of the GPE (black) and GPL (red). Reproduced from

C/3 rate (blue) for binding energy ranges analyzing Li1s and Nb4s (A),

F1s (B), O1s (C), C1s (D), Nb3d(E), and P2p (F). All samples were

washed with DMC to remove trace solvent and vacuum dried prior to

Figure 33: TNO vs. LMO cycling results for HDTe-2X1 at a rate of C/3 and a cutoff potential of 2.45V showing the capacity (A) and coulombic efficiency

- Figure 35: (A) TNO vs LMO full cells cycling in HTe-21 and HDTe-271. Upper potential cutoff and charge rate are 2.45V and C/3, respectively, unless stated otherwise. (B) Carbon coated TNO vs LMO full cells cycling to 2.80V. Comparison of HDTe-271 and HDO-12 electrolytes in TNO vs. LMO full cells cycling at a rate of C/3 and a potential cutoff of 2.45V (C) and 2.80V (D). Charge/discharge (E) and dQ/dV (F) plots of the first two cycles of carbon coated TNO vs LMO full cells cycling at a rate of C/3 and a potential cutoff of 2.80V.
- Figure 37: CV scans used a metal foil working electrode, activated carbon counter electrode, and Ag/AgCl reference electrode at a scan rate of 0.5 mV/s.
 Low voltage scan of HTe-21 (A) and HDTe-271 (B). High voltage scan of HDTe-271 first cycle metal foil summary (C) and detailed first three cycles for SS (D), Al (E), and Ti (F).

Figure 38: XPS spectra of cycled carbon coated TNO cells after cycling at a rate of
C/3 with an upper cutoff potential of 2.80V using HTe-21 (green), HDO-
12 (yellow), HDTe-241 (red), and HDTe-271 (blue). Elements of interest
are shown including Li1s and Nb4s (A), C1s (B), O1s (C), F1s (D), P2p
(E), N1s (F), and S2p (G)70
Figure 39: Fitted XPS spectra for carbon coated TNO cycled at C/3 at a cutoff
potential of 2.80V vs. LMO in HDTe-271 showing elemental signatures
for Li1s (A), C1s (B), O1s (C), and F1s (D)
Figure 40: XPS spectra of pristine carbon coated TNO (red), carbon coated TNO
cycled in HDTe-271 with a C/3 rate and a cutoff potential of 2.45V (blue)
and 2.80V (green). Elemental signatures are shown for L1s and Nb4s (A),
C1s (B), O1s (C), F1s (D), and Nb3d (E)72
C1s (B), O1s (C), F1s (D), and Nb3d (E)
C1s (B), O1s (C), F1s (D), and Nb3d (E)
C1s (B), O1s (C), F1s (D), and Nb3d (E)
C1s (B), O1s (C), F1s (D), and Nb3d (E)
 C1s (B), O1s (C), F1s (D), and Nb3d (E)
 C1s (B), O1s (C), F1s (D), and Nb3d (E)
 C1s (B), O1s (C), F1s (D), and Nb3d (E)
 C1s (B), O1s (C), F1s (D), and Nb3d (E)
 C1s (B), O1s (C), F1s (D), and Nb3d (E)

cutoff of 2.9V (red) marking maximum expected capacity. WIS21 with a

cutoff of 2.5V (purple). HTe-21 with a cutoff of 2.5V (brown), 2.6V

(green), and 2.7V (blue)	78
-------------------------	---	----

- Figure 47: (A) PNO half-cell in LP57 with a charging current of 20 μ A. (B) PNO and
 - (C) TNO full cells with an LMO cathode and HDTe-271 electrolyte
 - following a CCCV charging protocol at a rate of C/3 at a 2.45V (red) and
- Figure 49: Cycling results of a coated LTO vs LMO pouch cell using WIS21 (blue) and a control LTO vs LMO cell (purple) with PFOAn structure shown. 87
- Figure 50: (A) Comparison of PNO and C-PNO anodes using HDTe-271 at 2.45V and 2.60V cutoff potentials. (B) C-PNO full cells using HDTe-271 cycled

C-TNO vs LMO full cells. (B) CE for 2.8V electrolyte summary. (C)

List of Abbreviations

- AC Activated Carbon
- ALIB Aqueous Lithium-Ion Battery
- ASSB All-Solid-State Battery
- BAPO Bisacrylphosphine Oxide (Phenylbis(2,4,6-Trimethylbenzoyl)Phosphine Oxide)
- BETI Bis(Pentafluoroethanesulfonyl)Imide (N(SO₂CF₂CF₃) $_{2}$)
- BTFE Bis(2,2,2-Trifluoroethyl) Ether
- C-W-GPE Concentrated WIBS GPE
- CCCV Constant Current-Constant Voltage
- CE Coulombic Efficiency
- CEI Cathode Electrolyte Interphase
- CV Cyclic Voltammetry
- DMC Dimethyl Carbonate
- DMPA 2,2-Dimethoxy-2-Phenylacetophenone
- DSC Differential Scanning Calorimetry
- EC Ethylene Carbonate
- EDS Energy-dispersive X-ray Spectroscopy
- EIS Electrochemical Impedance Spectroscopy
- EMC Ethyl Methyl Carbonate
- ESW Electrochemical Stability Window
- EV Electric Vehicle
- FEC Fluoroethylene Carbonate
- FEMC 2,2,2-Trifluoroethyl Methyl Carbonate
- GPE Gel Polymer Electrolyte

- GPL Gel Protection Layer
- HANE Hybrid Aqueous/Non-Aqueous Electrolyte
- HDFA Heptadecylfluorodecyl Acrylate
- HEA 2-Hydroxyethyl Acrylate
- HER Hydrogen Evolution Reaction
- HFE Hydrofluoroether
- KIB Potassium-Ion Battery
- LIB Lithium-Ion Battery
- LCO Lithium Cobalt Oxide (LiCoO₂)
- LCP Lithium Cobalt Phosphate (LiCoPO₄)
- LFP Lithium Iron Phosphate (LiFePO₄)
- LHCE Localized Highly Concentrated Electrolyte
- LMFP Lithium Manganese Iron Phosphate (LiMn_{0.7}Fe_{0.3}PO₄)
- LMO Lithium Manganese Oxide (LiMn₂O₄)
- LNMO Lithium Nickel Manganese Oxide (LiNi_{0.5}Mn_{1.5}O₄)
- LSV Linear Sweep Voltammetry
- LTO Lithium Titanium Oxide (Li₄Ti₅O₁₂)
- LVPF Lithium Vanadium Phosphate Fluoride (LiVPO₄F)
- MA Methyl Acrylate
- MBD 4-Methoxybenzenediazonium Tetrafluoroborate
- MPEGA Methoxy Poly(Ethylene Glycol) Acrylate
- MV Multivalent Battery
- NBD-4-Nitrobenzenediazonium Tetrafluoroborate
- NCA Lithium Nickel Cobalt Aluminum Oxide (LiNi_{0.8}Co_{0.15}Al_{0.05}O₂)
- NIB Sodium-Ion Battery

- NMC Lithium Nickel Manganese Cobalt Oxide (LiNi_xMn_yCo_zO₂)
- NMP N-Methyl-2-pyrrolidone
- OCP/OCV Open Circuit Potential/Voltage
- $OTf Triflate (SO_3CF_3)$
- PC Propylene Carbonate
- PEO Polyethylene Oxide
- PEGDA Poly(Ethylene Glycol) Diacrylate
- PFOA Perfluoro Octyl Acrylate
- PNO Phosphorus Niobate
- PTFE Polytetrafluoroethylene
- PVA Polyvinyl Alcohol
- PVDF Polyvinylidene Fluoride
- SEI Solid Electrolyte Interphase
- SHE Standard Hydrogen Electrode
- TCA Thermoconductometric Analysis
- TEP Triethyl Phosphate
- TFEE 1,2-(1,1,2,2-Tetrafluoroethoxy) Ethane
- TFEO Tris(2,2,2-Trifluoroethyl) Orthoformate
- TFEP 1,1,2,2-Tetrafluoroethyl 2,2,3,3-Tetrafluoropropyl Ether
- TFSI Bis(Trifluoromethylsulfonyl)Imide (N(SO₂CF₃)₂)
- TGA Thermogravimetric Analysis
- TMP Trimethyl Phosphate
- TNO Titanium Niobate (TiNb₂O₇)
- UV Ultra-Violet
- VC Vinylene Carbonate

W-GPE – WIBS GPE

- WIS "Water-in-Salt" Electrolyte
- WIBS -- "Water-in-Bisalt" Electrolyte
- $XPS-X\text{-}ray\ Photoelectron\ Spectroscopy}$

Chapter 1: Introduction

<u>1.1 Lithium-Ion Batteries</u>

1.1.1 Market Demand

Lithium-ion batteries (LIBs) have slowly become an integral part of our everyday life. With just about everything now being battery-powered, ranging from heated socks to electric vehicles, society is surrounding itself with LIBs. Over the past thirty years, these batteries have grown in complexity and energy. And as the energy rises so does the focus on safety and cost. In 2021, the US Federal Government set a goal of 50% of all new vehicles sold in the US by 2030 to be zeroemission vehicles, a space largely dominated by electric vehicles (EVs).^[1] Several states, led by California, have even adopted a much more ambitious 100% goal by 2035. Even more ambitious considering that as of August 2022 the average EV cost \$66,524, with the battery costing as much as 50% of the total cost.^[2] Compared to the industry average of \$48,301, that is a 37% increase. Cost is not the only pressing factor, safety concerns are also a major consideration due to the difficulty of fighting EV fires. These two key reasons make it clear why cheaper and safer LIBs are of paramount importance.

1.1.2 Current State-of-the-Art LIBs

Rechargeable LIBs were conceived and developed during the 1980s before being commercialized in 1991.^[3] These early LIBs were not too different than our modern batteries, employing a carbonaceous anode, transition metal cathode, PVDF

binder, and an organic electrolyte containing a carbonate (PC) solvent and LiPF₆ salt. This first LIB was able to provide a specific energy of 80 Wh/kg and an energy density of 200 Wh/L at a cell voltage of 4.1V.^[4] This development was largely driven by the rise of the first portable electronic devices and the desire to reduce the size and weight of the batteries.^[3] Over the next 30 years, the LIB research field has made big improvements. Current state-of-the-art LIBs have the same basic components, a carbonaceous anode of graphite rather than soft carbon, a wider variety of transition metal cathodes (LCO, NMC, NCA) as well as spinel (LMO and LNMO) and phospho olivine (LFP, LMFP, LCP) cathodes, polymeric binders (PVDF, PTFE, Cellulose), and an organic binder predominately using carbonate solvents (EC, EMC, DMC, FEMC, etc.) with fluorinated salts (mostly LiPF₆ but also including LiTFSI and LiFSI) and various additives (VC, FEC, etc.). These modern batteries employed in current electric vehicles have cell level specific energies of 160-260 Wh/kg, energy densities of 450-730 Wh/L, and range in voltage from 3.6-4.0V+. Predictions and consortium goals are targeting >350 Wh/kg and >1000 Wh/L in the next few decades.^[5] While these state-of-the-art LIBs are a huge improvement and essential to modern society, theoretical material limitations, resource limitations/concerns on key elements like Li and Co, and safety issues arising from flammability concerns have created a need for alternative chemistries to better meet the growing demand for better rechargeable (secondary) batteries.

1.1.3 Alternative Secondary Batteries

There are now a wide variety of alternative battery chemistries to the dominant LIB. Each system has its own list of pros and cons. Metal anode batteries

(including Li, Ca, Zn, etc.) offer high energy density but pose many safety and stability problems. ASSBs (including polymer and ceramic electrolytes) offer improved safety and energy density but at the cost of increased material costs, low ionic conductivity, and poor calendar life. Alternate ion batteries (including NIB, KIB, Zn-ion, MV, and dual-ion batteries) have varying tradeoffs but overall are not yet mature enough to replace LIBs. And aqueous electrolytes provide another alternative and can be used in a variety of systems including polymer batteries, MV batteries, NIB, Zn-ion, and with typical LIB electrodes. ALIBs in particular are a promising alternative as they can easily be integrated with existing electrodes and additives with the added benefit of decreased costs and increased safety, an area not currently addressed by any systems shown in **Figure 1**.^[6]



Figure 1: (A) Relative strengths and weaknesses of various battery technologies including LIB, Na- and K-ion batteries (NIB and KIB), all-solid-state batteries, and multivalent batteries. (B) Calculations of various battery active materials using the BatPaC model. Reprinted with permission from [6]. Copyright 2021 American Chemical Society.

<u>1.2 Aqueous Lithium-Ion Batteries</u>

1.2.1 Birth of the ALIB

Aqueous lithium-ion batteries have been around almost as long as the original LIB. In 1994, Jeff Dahn led the research that produced the first published LIB utilizing an aqueous electrolyte.^[7] This system shared the use of a transition metal oxide cathode (LMO rather than LCO) but differed not only in the use of a 5M LiNO₃ aqueous electrolyte but also in the use of a much higher voltage anode of bronze-phase vanadium dioxide (VO₂ (B)). VO₂ (B) is about 2V higher in potential relative to the soft carbon anode used in the first LIB. It was necessary to pick an anode so much higher due to the much lower electrolyte. Water's electrochemical stability can be determined from a Pourbaix diagram (**Figure 2**). A Pourbaix diagram shows at what potential (relative to the standard hydrogen electrode (SHE)) an aqueous solution will break down based on various variables such as pH, temperature, pressure, and activity. The lines of stability (red dashed lines) are governed by the Nernst equation (**Eq. 1**)

$$E = E^0 - \frac{\ln(10) \cdot RT}{nF} \cdot \log\left(\frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}\right) - \frac{\ln(10) \cdot RTh}{nF} \cdot pH \qquad \text{Eq. 1}$$

When standard temperature and pressure are assumed, E^0 is set to 0V relative to SHE, and the fugacity of hydrogen gas is set to 1, the equation simplifies to **Eq. 2**

$$E = -0.05916 \cdot pH$$
 Eq. 2

This provides the lower stability line in **Figure 2**. For the upper stability limit, using the same assumptions as the lower stability line and using $E^0 = 1.229V$ for the oxidation of water, the equation simplifies to **Eq. 3**

$$E = 1.229V - 0.05916 \cdot pH$$
 Eq. 3

Between these two stability limits, water is electrochemically stable, but outside of them water will decompose based on the equations shown in **Figure 2**, giving a stability window of 1.229V. In a practical aqueous electrolyte, this electrochemical stability window can be extended due to changes in local pH, species' activities, and electrode passivation. The first ALIB had a voltage of 1.5V and provided 55 Wh/kg. While this was still short of even the first LIB (80 Wh/kg), it proved that reversible Li^+ electrochemistry could occur in water-stable systems.



Figure 2: Pourbaix diagram for water. Reproduced from Wikipedia.com.

1.2.2 Electrolyte Breakthroughs

In almost 20 years since the first ALIB, little had been done in order to dramatically change the ALIB. Much of the work addressed electrodes that were still within the standard electrochemical stability window (ESW) of aqueous electrolytes which resided between 1.2-2V.^[8] One of the major hurdles for ALIBs is the issue of electrolyte decomposition at electrode surfaces producing H₂ and O₂ gas. In organic LIBs, a good electrolyte can decompose into a protective layer on the electrode surface that prevents further side reactions. This protective layer is predominantly formed on the anode surface and is referred to as the solid electrolyte interphase (SEI) and is made of both organic and inorganic materials derived from the organic solvent, lithium salt, and any additives in the electrolyte.^[9] However, aqueous electrolytes are significantly hindered in that department since the decomposition produces hydrogen and oxygen gas. Therefore, if any SEI is to be formed, it needs to come from the salt or additives.

In 2015, a major breakthrough in ALIBs was made with the development of a new class of aqueous electrolytes, dubbed "Water-in-Salt" electrolytes (WIS).^[10] This electrolyte is now a part of a wider range of electrolytes of highly concentrated electrolytes where the electrolyte typically operates at saturated conditions for the salt. The first WIS electrolyte was composed of 21 m (mol of solute/kg of solvent) LiTFSI in water. Its unique properties allow for the extension of the ESW to 3V (**Figure 3**) thanks to the electrochemical reduction of the LiTFSI salt to produce an inorganic SEI rich in LiF. Using LMO as the cathode and Mo₆S₈ as the anode, a 2.3V battery was able to produce 84 Wh/kg.



Figure 3: (A) Reductive and (B) oxidative potential magnifications of (C) the electrochemical stability window for various aqueous LiTFSI electrolytes. Reprinted with permission from [10]. Reprinted with permission from AAAS.

In 2016, further improvements to the aqueous system provided incremental improvements with the addition of co-salts including LiOTf and LiBETI. ^[11, 12] The addition of the second salt increased the voltage and energy density to 2.5V with 100 Wh/kg and 2.3V with ~130 Wh/kg, respectively. And only two years after the last major ALIB breakthrough, Dr. Chongyin Yang demonstrated a 4V ALIB using LMO and graphite.^[13] Due to the aggressive reducing potentials required for the use of the low voltage anode, graphite, an anode protection layer was required to separate the aqueous electrolyte from the anode. This layer was composed of LiTFSI, PEO, DMC, and HFE (specifically 2,2,2-trifluoroethyl-1,1,2,2-tetrafluoroethyl ether) and required a modified aqueous electrolyte of LiTFSI, LiOTf, and PVA. The addition of the

polymeric components allowed for the physical separation of the two layers. However, the separation was not perfect, and mixing would eventually occur leading to cell performance degradation and failure. Furthermore, the incorporation of the HFE made the processing of this material impractical for commercial applications due to its extremely high volatility. With a cell voltage of 4V and similar electrode materials used as in LIBs, it was now shown that ALIBs had the potential to be competitive with state-of-the-art LIBs.

The next class of ALIB took a slightly different approach. Rather than introducing additional salts, the addition of co-solvents provided another promising alternative to the original WIS electrolyte. In 2018, Dr. Fei Wang developed a hybrid aqueous/non-aqueous electrolyte (HANE) with the mixing of saturated electrolytes of LiTFSI in water and LiTFSI in an organic solvent, dimethyl carbonate (DMC).^[14] The key benefits of this approach were the reduction of salt concentration (21m reduce to 13.3m), increased ESW (3.0V to 4.1V), and additional SEI generation from the carbonate component (Figure 4). Using LTO and LNMO, a 3.2 V cell was able to produce an energy density of 165 Wh/kg.



Figure 4: (A) Extended electrochemical stability window of the HANE electrolyte. (B) Cyclic voltammogram showing additional SEI formation process in early cycles. (C) Schematic of SEI formation from both salt and organic co-solvent. Reproduced with permission from [14].

The most recent evolution of ALIB electrolytes takes inspiration from localized highly concentrated electrolytes (LHCE).^[15-17] In LHCEs, a diluent, or non-solvating liquid, is added to the highly concentrated electrolyte to improve various properties such as viscosity, flammability, deposition, solvation, etc. (**Figure 5**). Originally this concept utilized organic electrolytes in Li metal batteries using hydrofluoroethers as the diluent; however, these hydrofluoroethers are not miscible with purely aqueous electrolytes. Therefore, an alternative diluent needed to be found. In 2021, several papers reported the use of a water-miscible cyclic ether that had a low dielectric constant resulting in very poor solvation of aqueous electrolyte salts (<0.2 m at room temperature).^[18-20] They found that the addition of 1,4-dioxane in sufficient quantities produced significant cycling and SEI improvements over the base 21m WIS electrolyte as shown in **Figure 6**. An insufficient amount of dioxane proved ineffective in providing cycling improvements in an LTO/LMO system.



Figure 5: (A) Schematic of dilution effect in LHCE. (B) Flammability test of glass fiber soaked separators. (C) Viscosity comparison of base highly concentrated electrolyte, LHCEs, and standard organic electrolyte. Reproduced with permission from [16]. Copyright 2018 Elsevier.



Figure 6: Discharge capacities and Coulombic efficiencies (CE) of LTO/LMO full cells. Reproduced with permission from [20]. Copyright 2021 American Chemical Society.

1.2.3 Aqueous Electrolyte Limitations

Each new iteration of the aqueous electrolyte has looked to address one or another of the limitations of ALIBs when compared to organic LIBs. The core issue limiting ALIBs from competing with LIBs in terms of energy density is what is referred to as the cathodic challenge.^[21] While several aqueous-based electrolytes report over 4V windows, the ESW is biased towards higher potentials and thus limits the availability of suitable anodes. This leaves ideal anodes such as lithium metal, graphite, and silicon unobtainable. Instead, the only readily available low-voltage anode material is LTO, which has an intercalation potential of almost 1.5V above lithium metal and graphite. In addition, while many electrolytes display excellent stability on metallic blocking electrodes during ESW tests, with real anodes, this working window is often significantly reduced due to premature electrolyte decomposition. This forces ALIBs to remain restricted to using LTO and often requires high cycling rates to mask cell degradation from electrolyte decomposition. The primary obstacle preventing ALIBs from reaching the lower potentials is due to the SEI layer that is formed not being robust enough to prevent water from reaching the anode surface and producing hydrogen gas. This low potential stability also results in issues with using standard coin cell components made of stainless steel and requires the anode side to be fully Al.

Another major obstacle is the high salt concentration required for the improved electrochemical stability. This creates two challenges in electrolyte viscosity and electrolyte cost. As the concentration increases, so does the solution's viscosity and with increasing viscosity comes decreases in transport properties and decreased wetting ability for separators. The latter requires the use of much thicker/heavier glass fiber separators compared to industry-standard polyolefin separators. With a thicker separator comes increased electrolyte and decreased cell level energy densities. And some of the ALIB electrolyte innovations, such as the bisalt and bi-solvent systems, only make this viscosity issue more pressing. The second issue is the cost. Aqueous LiTFSI electrolytes are an order of magnitude more expensive than standard LIB salt, LiPF₆, electrolytes. Part of this is due to economy of scale and with the adoption of LiTFSI electrolytes, the cost would go down. But the extremely high concentrations (almost 85wt% LiTFSI in 21m WIS) require a lot more salt than is found in the 1 M LiPF₆ organic electrolytes (13wt%). Each attempt to address this problem comes with a tradeoff. As mentioned with the HANE electrolyte, even though the concentration drops to 13.3m, the viscosity and transport properties are negatively affected; and with the use of dioxane, the safety benefit is lost due to dioxane's high flammability.

The third major challenge comes on the cathode side. At high potentials the typical metal material used for coin cells, stainless steel, begins to have corrosion issues with both organic and aqueous electrolytes, limiting the use of high-voltage class cathodes despite electrolyte electrochemical stability. In organic batteries, one solution is to use Al-clad coin cells to prevent this side reaction. Unfortunately, aqueous batteries are not able to take advantage of this as around 4.2-4.4V vs. Li/Li⁺ the aqueous electrolytes begin to corrode the Al. As seen in ALIB papers using LNMO, Ti current collectors and casings are employed for cell operation.^[12, 14] While this is important for advancing the science of ALIBs, it is not a practical solution and limits practical ALIBs to using lower voltage cathodes such as LMO, LCO, or NMC, which all come with their own issues and limitations.

The final limitation of the original WIS electrolyte is its temperature stability. While it was still able to operate at low temperatures, the solution exists on the saturation limit. A slight decrease in temperature can result in phase changes that alter several of the electrochemical properties and can result in partial crystallization of the electrolyte. This temperature instability enhances decreased cell performance as temperature declines. The addition of co-salts further exacerbates this problem while the addition of diluents and co-solvents alleviates some of these issues. Since practical battery usage is not limited to one constant temperature value, it is important to consider how the new electrolytes will respond to changes that fall within a reasonable usage window.

My dissertation aims to primarily address the first two limitations as in my mind, they are the two that limit the energy density of ALIBs the most, but the latter
two are improved as a consequence of electrolyte modifications. If a low-viscosity electrolyte has reasonable ionic conductivity (>1 mS/cm at room temperature), improved temperature stability, enhanced ESW, and decreased cost/salt concentration, while maintaining the ease of processability and safety features, ALIBs would become highly competitive. A tall order, but a goal the field is moving towards.

Chapter 2: Aqueous Gel Polymer Electrolytes

2.1 3V Gel Batteries

2.1.1 Introduction

One of the major breakthroughs for ALIBs was the use of aqueous polymer electrolytes to allow for phase separation of the aqueous electrolyte from the lowvoltage anode.^[13] We utilized PVA to essentially increase the electrolyte's viscosity without significant compromise to the ionic conductivity. The addition of the PVA further reduced the reactivity of the water and allowed for significantly enhanced stability of lithium metal, which normally will readily react with any water present, even atmospheric water. However, the stability was improved but not permanent and it was important to still keep water away from the anode surface. By adding an anode protection layer of LiTFSI in DMC (for ionic conductivity), PEO (as a plasticizer), and HFE (for hydrophobicity), we were able to physically separate the aqueous phase from the low-voltage anode. This allowed for the use of graphite and Li metal anodes to be used in a full cell that contained water without any physical membrane barrier (Figure 7). In addition to successfully cycling, these cells could even undergo nail penetration without suffering cell failure, highlighting the strong safety benefits of aqueous electrolytes and aqueous polymer electrolytes. Due to the lack of any chemical crosslinking and the disruption of any physical crosslinking from the high concentration of salt, the eventual mixing of the electrolyte would lead to cell degradation. Additionally, the high volatility of the HFE made this anode protection

layer nearly impossible to replicate at an industrial level. Nevertheless, this project laid an important foundation for the development of gel polymer electrolytes (GPE).



Figure 7: (A) 4V stability window of electrolyte. (B) Stabilization of graphite lithiation with the aqueous electrolyte. The voltage profile (C & E) and cycling stability (D & F) of LiVPO₄F vs. Li metal and graphite, respectively, at a rate of 0.3C. The capacity is based on the cathode mass. Reproduced with permission from [13].

2.1.2 Gel Polymer Electrolyte Development

The mechanical instability of this electrolyte not only was problematic in terms of cell performance, but it also posed a safety issue in the event of damage to the cell. When a cell is ruptured, the electrolyte can leak out. This is concerning because many of the electrolyte components, and side reaction/electrolyte degradation components, can pose health and safety risks if they get out, and it is one of the main reasons why you are not supposed to throw away your batteries in the normal trash. To get around this issue, the electrolyte would need to be used in a way that does not flow. Solid polymer and ceramic batteries are two ways of solving the problem, but they both come with their own plethora of challenges. Another method that is a simple evolution of the aqueous polymer electrolyte is to chemically crosslink the polymer to form a hydrogel that can prevent the aqueous phase from leaking out of the electrolyte. A crosslinked gel network not only contains the liquid phase, but also provides mechanical stability to prevent the mixing of the electrolyte with the anode protection layer. It also allows for the fabrication of freestanding batteries that can be designed in any shape and undergo a variety of mechanical stresses, most notably bending.

This proposed project was picked up as a collaborative project between Dr. Chunsheng Wang's lab at the University of Maryland, the US Army Research Laboratory, and the Johns Hopkins Applied Physics Laboratory.^[22] The initial challenge was to find a suitable crosslinked gel framework for the electrolyte. Building off the PVA system, I first attempted to crosslink PVA using a variety of crosslinking methods including physical methods (freeze-thaw) and chemical methods (glutaraldehyde). As mentioned previously, physical crosslinking is ineffective in the WIS class of electrolytes. Due to the extremely high salt concentration, the hydrogen bonding network is disrupted by the solvation of the salt. Chemical crosslinking methods were able to successfully create mechanically stable

16

GPEs, but the reaction speed was significantly retarded due to the high salt concentration. Thermal curing would take 2-5 days to completely cure the electrolyte depending on the exact crosslinker and polymer components. A faster method was needed.

Another method for forming polymer gel networks is through radical chain growth mechanisms. This method differed from the PVA system in that rather than using an already formed polymer and connecting them to make a network, mono- and multifunctional monomers were used to grow the polymer and crosslink it all in one step through the formation of reactive radicals. The gel growth could be initiated in a variety of ways, thermally activated, UV activated, or even electron beam activated. By utilizing this method with a UV curing step, I was able to reduce the curing time for the gel from days down to seconds or minutes depending on the exact composition of the gel electrolyte.



Figure 8: (A) Structures acrylate monomers (MPEGA₄₈₀ and HEA), diacrylate crosslinker (PEGDA₇₀₀), and photoinitiator (DMPA). (B) Schematic of crosslinked gel electrolyte showing both intra- and interchain crosslinking. The electrolyte would occupy the white space. Modified from [23].

Acrylates and methacrylates (**Figure 8**) were utilized due to their commercial availability with a wide array of functionality and the ability to also find multifunctional monomers that would be able to be utilized as crosslinkers. Other

chemistries were considered such as thiol-ene and did show promise as a likely alternative, but ultimately the acrylate/methacrylate chemistry was pursued.

As seen in **Figure 8B**, the monomers formed a crosslinked network using the electrolyte as the reaction medium. This meant that there would be no need to dry and reswell the gel, as it would already contain the desired electrolyte. One of the other benefits of using a GPE is that due to its mechanical strength, it could serve as both the electrolyte and the separator, thus removing the need for polyolefin or glass fiber separators.

For the first 3V aqueous GPE system, a UV-cured acrylate GPE utilizing the WIBS (21m LiTFSI + 7m LiOTf) demonstrated the concept of flexible ALIBs.^[22] The choice of acrylate was based on trying to find a gel network that would interact with free water molecules, thus further enhancing the electrolyte's ESW. Acrylates containing hydroxyl and ethoxy groups were ideal for this task. Methoxy poly(ethylene glycol) acrylate (MPEGA₄₈₀, M_n =480) and 2-hydroxyethyl acrylate (HEA) were selected as monomers with a difunctional crosslinker of poly(ethylene glycol) diacrylate (PEGDA₇₀₀, M_n = 700). This gave a gel that cured quickly and had the adhesive, elasticity, and strength properties that made for an easily processible GPE. These components were mixed in an 89:9:2 (wt%) MPEGA₀:HEA:PEGDA ratio to give the desired physical and chemical properties. It was also important to minimize the amount of polymeric components to ensure as high of an energy density as possible. It was found that a ratio of 75:25 (wt%) WIBS:Monomer mixture ratio allowed for GPE formation with an additional 0.5wt% of photoinitiator (DMPA or BAPO). This WIBS GPE (W-GPE) allowed for the extension of the ESW down to

1V vs. Li/Li⁺ (**Figure 9A**) with a satisfactory ionic conductivity of 0.6 mS/cm (**Figure 9B**). Another effect of the additional oxygen-containing functional groups in the GPE was that additional LiTFSI could be further dissolved creating a concentrated GPE (C-W-GPE), further extending the ESW. However, this additional LiTFSI hurt the ionic conductivity and increased the cost of the electrolyte and was unnecessary, as similar performance could be achieved using the lower concentration HANE electrolyte with the GPE.



Figure 9: (A) ESW of the base WIBS, W-GPE, and C-W-GPE. (B) Ionic conductivity of three different monomer formulations for W-GPE and C-W-GPE. Reproduced with permission from [22]. Copyright Royal Society of Chemistry 2019.

2.1.3 Gel Polymer Electrolyte Properties

In addition to the safety, mechanical flexibility/robustness, and the lack of a need for a separator, GPEs provide several other unique characteristics. Utilizing a novel analytical technique, GPEs could be measured in situ before and after UV curing.^[24] By placing Ni electrodes (adapted from a commercial conductivity cell YSI 3418) in a vertical arrangement inside of a hermetically fitted, UV-transparent

polypropylene bottle, thermoconductometric analysis (TCA) data was collected with excellent contact between the gel and electrodes. This method also allowed for a thorough analysis starting from infinite dilution of the polymer precursor up to 100% polymer precursor (**Figure 10**).



Figure 10: Photo of thermoconductometric cell with polypropylene bottle, nickel electrodes, and sample solution prior to UV radiation. Use of polypropylene bottle was ideal as it is UV transparent and can cut after curing to remove electrodes without damaging them. Reproduced with permission from [24].

The cell was calibrated with a KCl standard solution to determine the cell constant. The temperature differential signal ($\Delta\theta$) was determined using an identical test cell filled with propylene carbonate (PC) due to remaining in the liquid state for the entire temperature test range. Attached to the test cell and reference cell was a T-type thermocouple for temperature measurements. Temperature (θ) was controlled through a Tenney Jr. Engineering Environmental Chamber with a cooling scan at 0.1 °C/min followed by a heating scan at 0.1 °C/min. This slow rate would help to maintain thermal equilibrium for each measurement. Independent of the temperature scan, the temperature differential and impedance were continuously measured at the highest rate available. The impedance was collected with an Agilent E4980A Precision LCR Mater over the frequency range of 20 Hz to 2 MHz at a voltage

amplitude of 200 mV providing 150 readings per scan. The conductivity (κ) was calculated from the Nyquist plot of the impedance scan at the intersection of the curve with the real axis. This conductivity was paired with the temperature differential and temperature of the sample at the time of intersection, providing 1.2 points/min for the conductivity.

This analysis provided useful insight into the GPE design through a correlation of the liquidus phase change suppression upon cooling and a gel being produced upon curing. It also highlighted a unique property of a conductivity gain of the pre-gel:electrolyte solution after UV curing. In this study, the GPE was slightly modified to create a simpler 3-component system compared to the more complex GPE previously outlined. Here it is a mixture of the 21m WIS electrolyte with PEGDA₅₇₅ as a difunctional monomer that would allow for crosslinking and polymer growth with 1wt% 2-hydroxy-2-methylpropiophenone as the photoinitiator. As seen in Figure 11, when the mass fraction of PEGDA (w) increases above w=0.060, there begins to be a suppression of the freezing feature on the first scan towards lower temperatures, but the freezing feature is seen on the return scan, and the liquidus melting is also suppressed (Figure 12). This is due to creating a supercooled solution, which highlights the importance of scanning in both directions. More interestingly, this suppression appears to coincide with the compositions that can be classified as gels rather than liquids. Figure 11C shows the sample with w=0.230 which was one of the first samples that showed no phase change behavior, which correlated with the transition from gel to solid. Since it can be qualitatively difficult to differentiate

between the gel and solid boundary, this method could be used as a diagnostic tool to aid in electrolyte design when a gel composition is desired.



Figure 11: TCA curves of differential temperature (a) and conductivity (b) versus temperature for the pre- and post-UV samples with (A) w=0.060, (B) w=0.120, and (C) w=0.230. The baseline electrolyte (w=0) is plotted for reference. Sample was first cooled then heated at a rate of 0.1 °C/min. Reproduced with permission from [24].



Figure 12: Changes of liquidus (circles) and solidus (diamonds) temperatures with mass fraction *w* in the pre- and post-UV samples. Reproduced with permission from [24].



Figure 13: Conductivity gain upon polymerization, g_{κ} , as a surface (A) and contour plot (B). The contour lines represent 5% and all values lower than -20% collectively colored blue. The region for the gel is outlined in red. (C) Ionic conductivities of the *w*=0.120 GPE (blue pre-UV, red post-UV) compared to 21m WIS (black), liquid organic electrolytes with excellent conductivity (green, orange, and gold), and solid polymer electrolytes (brown and pink). Reproduced with permission from [25].

$$g_{\kappa} = \left(\frac{\kappa_{post-UV}}{\kappa_{pre-UV}} - 1\right) \times 100\%$$
 Eq. 4

The other takeaway from this experiment was the conductivity gain (g_x Eq. 4) increased by as much as 110% under certain conditions.^[25] Figure 13A,B highlights the set of compositions and the corresponding temperature regime where this conductivity gain upon UV curing occurs. Interestingly, almost the entirety of the gel region showed a conductivity gain below 0 °C (with the rest only having a 20% loss), and some of the largest gains were seen at very low temperatures for the soft solid compositions just beyond the gel region. While this gain is a large percentage change, due to the low absolute conductivity, this gain does not significantly improve the conductivity to compete with liquid electrolytes at these low temperatures (Figure 13C), but the GPE does show significant improvement in overall conductivity when compared to some traditional solid electrolytes. This conductivity gain goes against

the logic that the polymerization would create barriers to ion movement and indicates an underlying phenomenon that provides this result.

Through analysis of the glass transition temperature (θ_g), the detection of two glass transition temperatures provided the understanding to explain this conductivity gain. The glass transition temperature was measured using a differential scanning calorimeter (Discovery DSC 250; TA Instruments), with a liquid nitrogen cooler for low-temperature control. Hermetically crimped aluminum sample cells were quenched by dipping them into liquid nitrogen and then transferring the sample to a pre-cooled sample stage. The sample was then scanned up through its glass transition at a heating rate of 5 °C/min.

For w=0 to 0.060, only a single glass transition was observed that mostly reflected the glass transition of the 21m WIS liquid ($\theta_{g,s}$, **Figure 14A** blue region). When w=0.230 and greater, only a single glass transition was observed that mostly reflected the glass transition of the polymer ($\theta_{g,p}$, **Figure 14A** green region). However, for w=0.080 to 0.193, two glass transitions were observed that corresponded to $\theta_{g,s}$ and $\theta_{g,p}$. This result indicates that the GPE contains two molecular level substructures with a 21m WIS-dominated substructure and a polymer-dominated substructure. Within the gel region (w=0.080 to ~0.193), the two substructures are codominant, hence the two θ_g values. Inside the gel region, upon polymerization, the polymer substructure forms resulting in less remaining in the liquid substructure thus increasing the ionic conductivity in the post-UV samples when compared to the pre-UV samples. As *w* increases, the polymer substructure becomes overwhelming and creates barriers to ionic conduction and thus removes the conductivity gain and imparts a conductivity loss. This effect of the increasing w throughout the gel region and into the solid region is what gives rise to the bell curve feature shown in **Figure 14B**. The reason for the increased g_{κ} results from mathematical and scientific sources. Mathematically, since the conductivity decreases with decreasing temperature in the pre-UV sample and that term is in the denominator of **Eq. 4**, it produces a more dramatic effect. Scientifically, this can also be explained with the entropic term of free energy (T Δ S) favoring the more ordered state with a lower degree of entanglement between the polymer and solution substructures.



Figure 14: (A) DSC heat flow curves of post-UV GPE showing the two glass transition regimes of the solutionbased (blue) and the polymer-based (green). Red dots represent the glass transition temperatures ($\theta_{g,s}$ and $\theta_{g,p}$). The curves have been shifted on the vertical axis without affecting the θ_g values for visual clarity. (B) Combination plot of liquidus and solidus temperatures, glass transition temperatures (θ_g), and conductivity gains at selected temperatures, g_{κ} , as functions of mass fraction of PDA, *w*. The shaded regions represent the physical states of the GPE at room temperature. Reproduced with permission from [25].

The combination of all these properties provides a new and unique understanding of aqueous GPEs. This understanding can better classify GPEs as existing in the gel region or the soft solid region for optimal electrolyte design. GPEs offer unique advantages over all-solid-state electrolytes due to the ability to also offer the mechanical properties of a solid-like material but with the improved ionic conductivity of liquid electrolytes.

2.2 4V Gel Batteries

2.2.1 Introduction

Even with the improved ESW of the W-GPE, the lower cell voltage (3V class) limits its energy density and prevents it from being competitive with the organic LIBs. Extending the ESW of the electrolyte from \sim 1V (vs. Li/Li⁺) to graphite and lithium metal potentials (\sim 0.05V and 0V vs. Li/Li⁺, respectively) is of paramount importance if ALIBs are to be directly competitive with organic LIBs. The challenge remains that pushing a water-based electrolyte to even more reducing potentials is going to require extremely robust protection of the anode surface (and all conductive surfaces) from the electrolyte.

As previously mentioned with the 4V system from Yang et al.^[13], HFE provided an intriguing solution due to its high hydrophobicity and electrochemical stability at low potentials. In addition to being electrochemically stable and hydrophobic, this passivation layer needed to remain in place on the electrode surface and conduct lithium ions. HFE was mixed with 0.5m LiTFSI and 10wt% PEO and 5vol% DMC. The PEO served as a plasticizer to keep the liquid components from flowing away from the electrode surface. The LiTFSI and DMC were added to help with ionic conduction and lithium-ion solvation. This layer was the first generation of the anode gel protection layer (GPL). It allowed for coated lithium metal and graphite anodes to successfully cycle with both the published WIBS/PVA (10wt% PVA) (shown previously in **Figure 7**) and the later W-GPE. Even though water-based electrolytes could now be used with graphite and lithium metal, there were still several issues with this system that significantly hindered the building and testing of larger cells. The GPL was a thick paste that had to be coated on each electrode manually making larger cells hard to reliably fabricate. The GPL, though hydrophobic, would still slowly allow the water layer to penetrate after enough time which led to rapid cell failure, evident through reduced cycling efficiency (<99%) and poor cycle life. The HFE was extremely volatile and would rapidly evaporate during fabrication, making it impractical for roll-to-roll processing. There were also major issues with reproducibility. Less than 10% of cells built would be able to cycle due to the complexity of cell fabrication. This first GPL was also more of a protective layer than a true gel. Developing a crosslinked GPL based on the chemistry and understanding from the 3V system is a promising solution to several of the challenges faced by this initial attempt.

2.2.2 Gel Protection Layer

The first step was to replace the polymer components with the GPE (MPEGA, HEA, and PEGDA), denoted as G1. This allowed for a mechanically robust and UVcured protection layer that would not suffer from the mixing of the two layers. Changing to G1 also helped with the processing as the pre-gel solution could be uniformly coated onto the anode surface before being cured in a few seconds. Due to the difficulty of using HFE, an alternative GPL liquid phase needed to be selected. The initial choice was a 2.5m LiTFSI in PC with 3wt% FEC (denoted as P1). When contained within a glass fiber separator as extra insurance against electrical shorts and paired with the C-W-GPE, a full cell with LMO vs. graphite was able to cycle but with significant loss of capacity and fade (Figure 15A).



Figure 15: (A) Cycling data for LMO vs. Graphite using P1 soaked glass fiber separator and C-W-GPE. (B) Cycling data for LCO vs. Graphite using C-W-GPE and various GPL chemistries.

This initial system was not ideal due to the previously mentioned issues with the C-W-GPE conductivity and cost as well as the GPL's composition. PC is problematic on graphite and can lead to graphite exfoliation and rapid cell failure. Using a variety of different hydrophobic components, several GPL candidates were screened (Figure 15**B**). While the HDFA (heptadecylfluorodecyl acrylate) provided the most initial capacity, the rapid capacity fade and sudden cell failure indicated that this layer may not be fully stable and allowed water to eventually get to the anode surface and cause the cell to fail. On the other hand, P2 (1m LiTFSI in FEC/FEMC (1:1 wt%)) demonstrated lower initial capacity but significantly more stable cycling. This is most likely due to the fluorinated components preventing mixing with the aqueous phase and good SEI forming capabilities. Since the G1 pre-gel solution and P2 are fully miscible, the G1P2 GPL (here on referred to simply as GPL) could be easily coated onto the graphite surface for UV curing.

2.2.3 Full Cell: Materials and Methods

Due to the decreased concentration and improved ESW, a variation of the DMC-based HANE was used as the aqueous phase for the GPE.^[23] It was found that replacing DMC with a flame-retardant organic phase of trimethyl phosphate (TMP) provided more reliable cycling; in addition to removing the flammable component, the salt content could be further reduced from 13.3m to 9.5m (more detail on the development of the HANE system will be provided in 3.1 Hybrid Aqueous/Non-Aqueous Electrolyte. The TMP electrolyte (denoted as HT-29) was prepared by dissolving 9.5 mmol LiTFSI in 1 g water: TMP (2:9 mass ratio). The GPL electrolyte was prepared by dissolving 1 mmol LiTFSI in 1 g FEC:FEMC (1:1 mass ratio). The pre-gel solution used for both the GPE and the GPL was a mixture of MPEGA₄₈₀:HEA:PEDGA₇₀₀ with 0.2wt% DPMA photoinitiator. For the GPE, the components were mixed at a mass ratio of 89:9:2. Due to the GPL's different electrolyte consistency, an increased amount of crosslinker (PEGDA₇₀₀) was required and the GPL pre-gel solution was mixed at a mass ratio of 86:7:7. These pre-gel solutions were then mixed with the respective electrolyte at a mass ratio of 25:75 (pre-gel:electrolyte).

Graphite (95wt% Saft proprietary graphite, 5% PTFE binder, 1.1 mAh/cm²) vs. LCO (90wt% LCO, 5wt% PVDF binder, 5wt% carbon black, 1.2 mAh/cm²) pouch cells were assembled with an electrode area of 25.08 cm² (maximum theoretical cell capacity of 27.59 mAh). The respective pre-gel electrolyte solution was cast over the electrode at a thickness of 70 µm for a combined GPL-GPE thickness of 140 µm and a total cell stack thickness of 320 µm. Prior to UV curing,

29

the coated electrodes were placed in a vacuum chamber for 2 min to increase the amount of electrolyte in the electrode pores. To ensure a smooth and uniform surface, a PTFE-coated tape was placed on a glass slide to cover the electrode at the desired thickness. Since neither the glass nor PTFE tape blocked the UV light, the gel was able to be cured through the cover glass. The PTFE tape was used to prevent the adhesion of the cured gel to the cover glass. The electrode was then placed 6 cm from the mercury vapor UV lamp (180 mW/cm² power) for 60 s. The time was set to 60 s for two reasons, the first is that while the cover glass was transparent to UV light, it did absorb some and required an increased cure time. The second was to ensure the complete reaction of the pre-gel solution. Any unreacted monomer could mix with the liquid phase and participate in unwanted side reactions. There was one additional step for the anode, a Celgard 2400 polypropylene separator was placed over the anode prior to the addition of the pre-gel GPL solution. While this is not necessary, it was done to prevent possible electrical shorts for diagnostic purposes. The two electrodes coated in the GPE and GPL were there placed together and the adhesive properties of the gels held the two cell halves together. The pouch cell was then vacuum sealed for 30 s. The entire assembly process is summarized below in Figure 16.



Figure 16: (A) Assembly process of the 4V Aqueous GPE pouch cell. (1) Electrode is placed in mold to control electrolyte thickness, (2) pre-gel electrolyte is added, (3) pre-gel electrolyte is placed under vacuum to promote electrolyte filling into the electrode pores, (4) PTFE tape covered glass is placed on top of mold, (5) mold is placed into the UV chamber for 60 s irradiation, (6) electrode is removed from the mold, (7) cathode and anode are combined, (8) cell stack is vacuum sealed in pouch cell. (B) Schematic of cell stack showing thicknesses. Reproduced from [23].

Material characterization and cell performance were conducted using thermogravimetric analysis (TGA), UV-modulated rheology, UV/Vis spectrometry, electrochemical impedance spectroscopy (EIS), and battery cycling. The TGA was conducted on a TA Instruments TGA 550 with a temperature range from room temperature (RT) to 250 °C at a ramp rate of 10 °C/min. The UV-modulated rheology used a TA Instruments Discovery HR-2 rheometer with an OmniCure Series 2000 UV/Vis curing accessory. The GPE and GPL gelation processes were recorded at RT with a 320-480 nm irradiation source set to 180 mW/cm². An oscillatory strain of 10% and a frequency of 1 Hz were used, with irradiation set to begin 30 s after experiment initiation. UV/Vis spectrometry was conducted using an Avantes AvaSpec 2048L detector and StellarNet deuterium/halogen source (190 nm 1100 nm). Samples were placed in 350 µL Thor Labs fused quartz cuvettes. EIS testing was performed on a Solartron 1276/1280 device pair with all cells in the discharged state to allow for comparison between pre-cycled and cycled cells. Cells were scanned through a frequency range of 1 MHz - 1 Hz at an amplitude of 10 mV with respect to the cell's open circuit potential (OCP). Battery cycling was conducted on a Maccor 4000 battery tester with a constant current-constant voltage (CCCV) test routine. Cells were initially tap-charged to 1V, then allowed to rest for 3 h. Cells then underwent two CC-only forming cycles at a C/10 rate from 4.2V to 3.2V. Once formation was complete, the cells cycled at C/10 from 4.2V to 3.4V followed by a constant voltage charge/discharge at the limit until either a current of C/50 was reached or 2 h had elapsed. Pouch cells were placed in cell holders with an applied pressure of ~2 psi.

32

2.2.4 Full Cell: Results and Discussion

Polymerization had three primary factors affecting the rate in this system including the following: solubility of monomers, UV absorption by the electrolyte, and viscosity effects. In addition to the previously stated reasons for selecting MPEGA, HEA, and PEGDA, their ability to be soluble in both the 21m WIS and the anode protection layer made them ideal candidates for this system. The source used UV radiation primarily emitted in the 300 nm-400 nm range (Figure 17A) where the DMPA photoinitiator demonstrated an extended absorption region.^[26] Solvent absorption is evident for the GPL electrolyte (FEC:FEMC) as seen by the stronger absorption band in Figure 17B when compared to the GPE electrolyte (Water:TMP). This additional absorption by the GPL electrolyte could lead to decreased initiation rate with an additional rate reduction caused by protonated carbonyl acting as a radical scavenger.^[27] These two effects were readily seen in the need for additional crosslinker content in the GPL and the rheology results. Due to the slower kinetics in the GPL, the increased crosslinker content was needed to increase the chances of successful crosslinking in the slower polymerizing system.



Figure 17: (A) UV-Vis spectra of HT-29 GPE electrolyte (black), 1m LiTFSI in FEC:FEMC GPL electrolyte (red), 0.01% DMPA in water (green), and the UV source. (B) 300-400 nm close-up. Reproduced from [23].

UV-modulated rheology is a useful technique for gel analysis as it gives information about the time to form a gel and its elastic character. Gel formation can be indicated by when the storage modulus (G') and loss modulus (G'') intersect, also known as the modulus crossover (G'/G''=1).^[28] For the GPE, this occurs after 7.3 s while the GPL takes 32.3 s, almost 4.5x slower than the GPE (Figure 18). Based on the lower viscosity of the GPL precursor, it would be assumed that the kinetics of gel formation would favor the GPL; however, as previously stated, the UV absorption by the GPL solvent hinders the kinetics, leading to this increased gelation time. Also plotted is the complex viscosity, this is simply a measure of the resistance to flow. It can also be characteristic of the transition from liquid to solid as the sharp increase in this value indicates rapidly changing viscosity (gelation) and a plateau after a rapid change can be indicative of a change to a solid/gel state. It can be seen that after the crossover point, the complex viscosity begins to transition from a linearly increasing slope to a flat plateau, indicative of the transition from a solution to a gel in this system. Another useful result of the rheological study was obtaining the plateau modulus. This is obtained by measuring the steady-state storage modulus (G') at t=3000s. Ideally for a "soft" gel electrolyte, a low storage modulus (in the kPa to MPa range) is desired. The plateau modulus for the GPE was found to be \sim 33 MPa and for the GPL it was found to be \sim 740 kPa.



Figure 18: UV-modulated rheology analysis for the GPE (A) and GPL (C) with close-ups of the modulus crossover for the GPE (B) and GPL (D). Reproduced from [23].



Figure 19: TGA analysis of the GPE (black) and GPL (red).

TGA analysis showed limited mass loss up to 100 °C with 2% for HT-29 and 11% for the GPL electrolyte (**Figure 19**). The rapid loss in mass of the GPL electrolyte after 100 °C is due to the loss of FEMC leading to a rapid increase in the cell's internal pressure and increasing the chances of cell rupture. Cell operation

below this point, between 70-90 °C, would provide significantly improved hightemperature performance potential compared to state-of-the-art organic electrolytes that suffer cell performance issues when operated near 70 °C.

The liquid HT-29 electrolyte has an ionic conductivity of around 0.8 mS/cm at room temperature.^[29] As previously shown, the incorporation of an electrolyte into a GPE decreases the ionic conductivity of the electrolyte.^[24] In the HT-29 GPE, the conductivity drops to 0.3 mS/cm but remains acceptable (**Figure 20**). The GPL's electrolyte has an ionic conductivity of about 3 mS/cm and drops to around 1.3 mS/cm when gelled into the GPL. At higher temperatures, the gel electrolytes deviated from Arrhenius behavior due to the slow loss of electrolyte. This effect is more noticeable in the GPL due to the increased loss of FEMC.





Traditional electrodes are designed with pores to allow for the electrolyte to permeate through and provide intimate contact with the entire electrode material. A porous electrode is not ideal for the GPE. As previously mentioned, to try to alleviate this issue, a vacuum fill step was employed along with in-situ UV polymerization of the gel in the electrode. **Figure 21** demonstrates that it was possible to achieve 62% of the cell capacity on first discharge in a 4V class aqueous-based electrolyte battery (17.1 mAh out of a possible 27.6 mAh). While not all of the capacity was achieved, this marked an important step forward in the fabrication and performance of aqueous GPE batteries. Within 10 cycles, CE was able to reach over 98% and remained stable for several cycles before declining. This initially high CE is indicative of preventing water from reaching the anode surface. This is due to the robust LiF-rich SEI formed by the hydrophobic GPL layer electrolyte.^[30] The subsequent performance decline can then be attributed to the less-than-ideal contact between the GPE/GPL and electrodes and potential corrosion issues on the cathode side between the aqueous phase and the Al current collector (this will be discussed more in **Chapter 3**:







Performance and safety are key aspects of this system. In addition to the above performance results, the 4V GPE cell demonstrated several safety benefits. The GPE allows for physical damage to the cell by cutting the cell with scissors during operation without producing cell failure. This is due to the ability of the electrolyte to resist the temporary electrical short created by the scissors and the solid-like properties of the GPE preventing the electrolyte from leaking out. The GPE allows for some strain in excess of 5% and has a low storage modulus of 3-3.5 kPA. The combination of these two properties allows for the physical deformation of the cells without exposing the bare electrode to potential electrical shorts. The non-flammable and higher temperature stability of the GPE also allows for safer operation in more extreme conditions with a reduced risk to battery safety.

After the initial publication of this work, the project's focus on practical considerations for transitioning to industry has been realized. An industry partner has been able to scale up with reproducible results. They have successfully built the 4V system using a graphite anode, LCO cathode, HT-29 GPE, and FEC:FEMC GPL, with only minor modifications to adjust for processing scale-up challenges. The cells have also successfully survived penetration testing without catastrophic failure and only a minor temperature increase.

This study's results are important for creating a foundation for safe, highenergy flexible batteries that will become increasingly crucial in the future of wearable electronics.

38

Chapter 3: Electrolyte Modification

3.1 Hybrid Aqueous/Non-Aqueous Electrolyte

3.1.1 Introduction

While the GPE demonstrated the ability of aqueous electrolytes to offer enhanced functionality in a safe manner and with additional electrochemical stability, it does come with tradeoffs in ionic conductivity, electrode utilization, and processability. Additionally, the high voltage 4V GPE battery still requires the use of an organic protection layer in order to function against graphite. While it may not be possible to ever fully allow aqueous-based electrolytes to directly interact with graphite anodes, it is possible to improve the performance at lower and lower potentials for when alternatives to graphite become available at slightly higher potentials. It is also important for the improvement to be implemented in the current 3V range that aqueous electrolytes have been demonstrated to work without additional protection layers to become a cheaper and safer alternative to low-voltage organic systems. With this project, I explore some of the issues that need to be addressed to maximize aqueous-based electrolyte performance. It is challenging to be able to address performance, cost, and safety all at once, therefore I will attempt to focus on identifying the challenges that need to be further investigated rather than offering a final all-encompassing solution. Initially, I investigated the HANE system^[14] in more detail due to the familiarity with it from previously using it in the GPE study.

39

3.1.2 Organic Phase Replacement

The first generation of HANE consisted of a mixture of two saturated electrolytes of LiTFSI – a 21m aqueous electrolyte (WIS) and a 9.3m organic electrolyte using DMC.^[14] The exact ratio of these two electrolytes was a compromise between electrochemical stability, cycling performance, viscosity, and ionic conductivity. It was found that a 13.3m electrolyte with a 2.5:1 molar ratio of water to DMC provided optimal results (this electrolyte will be referred to as HD-251 where the letters refer to the solvents and the numbers refer to the molar ratios, respectively). Due to the high concentration, the two normally immiscible solvents were able to form a homogenous solution that retained the non-flammable benefits of the aqueous electrolyte. This first generation of hybrid electrolytes had issues with quickly achieving stable cycling (after 50 cycles), cycle life, and the ever-looming concern of a flammable component in the electrolyte.

Many alternatives have been demonstrated including but not limited to acetonitrile^[31, 32], sulfolane^[33], dioxolane^[34], poly(ethylene glycol)^[35], urea^[36], and TMP^[29]. Each system comes with its own set of pros and cons. With a focus on non-flammability, the use of trialkyl phosphates has been readily shown to be effective as flame-retardant components in organic electrolytes^[37-42]. TMP has already been used in the GPE system and has recently been demonstrated in a traditional liquid ALIB; however, it does come with safety concerns in terms of acute oral toxicity (category 4), skin corrosion/irritation (category 2), serious eye damage/eye irritation (category 2), germ cell mutagenicity (category 1B), and carcinogenicity (category 2). With aqueous electrolytes being advertised with a big emphasis on safety, I wanted to try to

find an alternative that would reflect that while maintaining the positives that the TMP hybrid provides.

Triethyl phosphate (TEP) is closely related to TMP but with the only hazardous warning listed as acute oral toxicity (category 4), which is the same as TMP, but all of the other hazards are not present. Additionally, TEP offers stronger flame-retardant properties^[39] and a lower salt concentration while maintaining comparable electrochemical performance. The TMP electrolyte previously mentioned is a mixture of saturated solutions of LiTFSI in water and TMP with an approximate molar ratio between the water and TMP of 1.73:1. Trying to maintain similar solvation structures, I did an approximate mole-to-mole replacement of TMP with TEP by mixing saturated solutions of LiTFSI in water (21m WIS) and TEP (5.5m LiTFSI in TEP, referred to as TIS) with a molar ratio of 2:1 between water and TEP, respectively. This provided an 8.06m LiTFSI in water and TEP electrolyte (HTe-21, Te is used to represent TEP to differentiate from TMP).

3.1.3 TEP Hybrid Electrolyte Results and Discussion

Linear sweep voltammetry was first run on both the base 21m WIS (WIS21) aqueous electrolyte and the 8.06m LiTFSI in Water/TEP (HTe-21) hybrid electrolyte using a Biologic SP-150 potentiostat. The working electrode was Al foil, and the counter electrode was activated carbon (AC) with an Ag/AgCl reference electrode. All Al working electrodes were cut to a uniform 1 cm² area for comparison of current between samples. Scans were conducted at 0.5 mV/s. The choice of Al foil for the working electrode was a necessity for the cathodic scan due to the stability of the metal substrate with the electrolyte and to match the material used in test cells. It was also used for the anodic scan even though it suffers from corrosion in the highly concentrated LiTFSI aqueous electrolytes as seen in the LSV for WIS21 at around 4.3V (Figure 22). This decision was because despite Ti being more stable, Al and stainless steel (SS) are still the most practical metal components for batteries due to cost and weight. The ESW shown should not be taken as the true ESW, but instead as a practical ESW for the materials present in the test coin cells. The HTe-21 extends the decomposition limit of the electrolyte from 1.9V to 1V and significantly reduces the Al corrosion current on the higher end. While the ESW is also extended at higher voltages, it is not discussed here due to using Al foil and the complicating factor of Al corrosion. These combined effects both contribute to the ability of the hybrid electrolytes to fully encompass previously inaccessible anodes in the aqueous electrolyte (e.g. LTO) and to improve the CE due to the improved stability corrosion.



Potential (V vs. Li/Li⁺)

Figure 22: LSV of WIS21 (blue) and HTe-21 (red) with Al working electrode, activated carbon counter electrode, Ag/AgCl reference electrode, and a scan rate of 0.5 mV/s. Each LSV was done in two scans, one from OCP to -3V vs. Ref and another scan from OCP to +3V vs. Ref.

While the ESW of the HTe-21 is significantly improved, the cost comes out of the conductivity which takes a very large hit dropping from 8 mS/cm for WIS21 to 0.6 mS/cm in the HTe-21 (Figure 23A). This lower conductivity does hurt the cycling performance of the electrolyte. Figure 23B shows the 1st cycle for two TNO vs. LMO full cells using the WIS21 and HTe-21 electrolytes (further discussion of the anode selection of TNO will be detailed in Chapter 4: Anode Modifications). The lower conductivity of the HTe-21 leads to an overpotential growth as seen by the purple curve's higher charging profile and lower discharging profile. This can be alleviated through the use of a constant current-constant voltage (CCCV) charging profile. During the constant current charge, the HTe-21 reaches 95 mAh/g while the WIS21 reaches 113 mAh/g. Allowing for a constant voltage charge, the slower kinetics of the HTe-21 is allowed to catch up and both cells finish the charging cycle with 115 and 118 mAh/g, respectively. On discharge, they both reach a discharge capacity of 105 mAh/g, yielding a CE of 90.88% and 88.55%, respectively. The improved CE is a little counterintuitive based on conductivity alone but makes sense when the Al corrosion issue is considered and the improved stability of the HTe-21.



Figure 23: (A) Conductivity values for WIS21 (blue), HTe-21 (purple), and a reference organic electrolyte LP57 (red). Values obtained using TCA as previously described. ^[24] (B) 1st cycle charge/discharge of TNO vs. LMO at C/3 with a CCCV charging protocol and a 2.45V cutoff.

By adding in the TEP as a saturated solution, the bonding environment of the water does not change as observed in the FTIR spectra of increasing WIS concentrations and the hybrid (Figure 24). The primary issue for the aqueous electrolytes is the presence of water at the electrode surface. Upon addition of LiTFSI, the -OH stretching vibration above 3000 cm⁻¹ begins to shift from predominantly water-water interactions (2W, centered just below 3300 cm⁻¹) to water-water-anion interactions (1W+1a, centered around 3400 cm⁻¹) to predominantly anion-water-anion interactions (2a, centered around 3550 cm⁻¹) and free water (no Hbonding, centered around 3625 cm⁻¹).^[29, 43] The shift of the water bonding environment from hydrogen bonds (H-bonds) to exclusively other water molecules shifting toward the salt ions is part of the reason for the improved stability.^[10] Given that the TEP does not shift shape indicates that the water remains in a similar solvation structure that promotes stability. The decrease in peak intensity is related to the decrease in overall water content in the electrolyte. This reduction of overall water may be one of the reasons the hybrid electrolyte offers improved stability over WIS21 since less water is brought to the surface during intercalation.

The hybrid electrolyte was tested and compared to the aqueous and organic electrolytes using TNO vs. LMO full cells. The LMO cathode was used as prepared from Argonne National Laboratory with an areal capacity rating of 1.17 mAh/cm² on Al foil. TNO anodes were prepared from in-house synthesized TNO with and without a carbon-coating (2wt% acetylene black), conductive carbon (30wt% carbon nanotubes and 70wt% Timcal C45), and PVDF binder. The anodes were prepared in an 80:10:10 mass ratio in an NMP slurry. The TNO slurry was cast on Al foil to

44

provide a cathode excess capacity in the range of 20-40%. Stainless steel 2032 coin cells were used to assemble the cells. As mentioned, the anode side was made to be completely Al either through the use of Al-clad cell cases or the use of a piece of Al foil to line the SS cases. One wave-form spring and two 0.5 mm spacers were used to provide consistent pressure across cells and a quartz microfiber (QMA) separator was used to prevent internal electrical contact between the electrodes. Approximately 100-150 μ L of electrolyte was added (the amount varied depending on the viscosity of the electrolyte in order to minimize electrolyte leakage while ensuring sufficient electrolyte to flood the cell).



Figure 24: FTIR spectra of DI water (blue), 10m WIS (green long dash + two dots), 15m WIS (green short dash), 21m WIS (green solid), neat TEP (red), and HTe-21 (purple). Variations in -OH vibrations are labeled based on solvation environment.

Cycling procedures were conducted on a Maccor 4000 battery tester. The testing protocol was a CCCV charge and constant current discharge between 1.5V and the upper cutoff, ranging from 2.45-3.0V. The current rate was set by the mass of anode active material using a theoretical TNO capacity of 230 mAh/g and the

constant voltage charging cutoff was set to a current threshold of C/20. This capacity is the capacity that is achievable at a C/10 rate in an organic electrolyte in a TNO vs. Li metal half-cell when cycling between 1.0-2.5V. In full cell ALIBs, the TNO full capacity is not achievable in the voltage range safe to cycle in, but this value was used for the purpose of uniformity and simplicity when switching between rates, voltage cutoffs, and electrolytes. Anodes were vacuum-dried before weighing and all cells were assembled under ambient atmosphere. Cells were allowed to rest for 12 hours prior to the start of cycling. Due to the benefit of having water-tolerant electrolyte components and an overall aqueous-based electrolyte allows for cells to be assembled under ambient conditions rather than in costly dry rooms and glove boxes, due to typical organic electrolyte reactivity with even trace amounts of water. This assembly method highlights one of the cost-reduction factors of the ALIB system.

When directly compared to WIS21, the hybrid electrolyte, HTe-21, offers some key benefits with only minimal tradeoffs (**Figure 25**). WIS21 offers improved ionic conductivity and viscosity properties when compared to the HTe-21 and this can most readily be seen in the rate cycling ability of the two electrolytes (**Figure 25A,B**). Due to electrolyte instability on the anode and the Al foil on the cathode, both electrolytes show capacity fade at the slow rate of C/10 (red plot). Upon rate increase to C/3 (orange plot), the CE and cycling performance are improved as the system is able to push past these failure mechanisms. Further rate increase to 4C (purple plot) shows the benefit of the CCCV charging profile to maintain the capacity, but upon discharge, the HTe-21 shows considerable loss of capacity due to the limitations imposed by the lower ionic conductivity and higher viscosity. **Figure 25C** demonstrates the increased instability upon increasing cutoff potential even a small amount from 2.45V to 2.50V. There is a noticeable CE decrease due to allowing these detrimental side reactions to occur that negates and even decreases any capacity gains gained by increasing the cutoff potential to try to use more of the available capacity in the TNO anode. However, the effect on the HTe-21 is diminished compared to the WIS21 thanks to the improved ESW and reduced Al corrosion.

Upon increasing the cutoff to 2.80V with a carbon-coated TNO anode, the benefit of the HTe-21 can be seen even better when compared to the WIS21 (**Figure 26A**). With the LP57 results as the benchmark for these conditions, the HTe-21 shows excellent discharge capacity on the first cycle for an ALIB, achieving 181 mAh/g, the highest reported based on the mass of anode active material. Obtaining 95% of the expected capacity based on 190 mAh/g for the LP57. With an improved CE of up to 97.5%, the HTe-21 is able to retain 77% of its initial discharge capacity after 40 cycles and 57% after 100 cycles. When compared to the CE of 99.9% for the LP57 and a capacity retention of 99%, there is still a lot of room for improvement, but when compared to WIS21 (65 mAh/g first cycle discharge, 8% first cycle CE, 42% capacity retention after 40 cycles and 36% after 100 cycles), it is clear the immense benefits offered by hybrid electrolytes and specifically the HTe-21.



Figure 25: TNO vs. LMO full cells cycling with an upper voltage cutoff of 2.45V at various C-rates in (A) WIS21 and (B) HTe-21. Arrow indicates the effect of increasing the C-rate from C/10 to 4C. (C) Full cells with WIS21 at 2.45V (red), 2.50V (black) cutoff and HTe-21 at 2.45V (blue), 2.50V (purple) cutoff.


Figure 26: (A) Capacity (circles) and CE (triangles) data for 2.80V cutoff at C/3 using C-TNO vs. LMO in WIS21 (red), HTe-21 (orange), and LP57 (green). (B,D,F) 1st and 2nd charge/discharge cycles for LP57 (B), HTe-21 (D), and WIS21 with insert showing the full constant voltage charge plateau (F). (C, E, G) dQ/dV plot for select cycles for LP57 (C), HTe-21 (E), and WIS21 (G).

The charge/discharge curves and dQ/dV plots of these three cells illuminate some of the reasons for the differences in performance. Figure 26B,C shows the typical performance of the LP57 electrolyte. Due to the excellent ionic conductivity and viscosity, a very short constant voltage charging is required and changes between cycles are minimal as noted by the similar constant voltage charging length and the minor change to the dQ/dV intercalation peaks. In the HTe-21 (Figure 26D,E), the significantly longer constant voltage charging phase, well in excess of the recovered discharged capacity, highlights the electrolyte instability at these conditions. Furthermore, the large shift in intercalation peaks on the charging phase (positive dQ/dV peak) is indicative of electrolyte decomposition and overpotential growth. Continued peak shifting indicates that this process is ongoing throughout the lifetime of the cell. WIS21 shows an even bigger deviation from the benchmark (Figure **26F,G**). The first cycle charging curve has a second inflection point indicating an additional process before the extremely large constant voltage charging (seen in the insert). The first cycle records a charge capacity of over 850 mAh/g, which is well higher than the LP57 benchmark and is a strong indication of electrolyte decomposition. This is further verified in the dQ/dV plot showing a second peak just under 2.8 V. This massively shifts the intercalation peak on the second cycle. Continued decomposition and side reactions lead to the eventual suppression of this intercalation peak and the failure of the cell.

This marks the first documented use of the TNO anode in an ALIB producing a benchmark-setting initial discharge capacity of 180 mAh/g at 2.8V. While this still falls well below the LP57 performance, ground can be made up through optimization of electrode coatings, electrolyte composition adjustment, incorporation of additives, and replacement of SS and Al coin cell components on the cathode side with Ti. These changes have the potential to produce a more competitive system, but at the loss of reduced costs. Instead, further development of the electrolyte could offer improved performance under the same cell construction and cycling conditions without relying on expensive Ti cell components.

3.2 Electrolyte Diluent

3.2.1 Introduction

Highly concentrated electrolytes have proven very capable of expanding the electrochemical window for aqueous electrolytes and improving corrosion issues. They have also found use in organic systems in providing for reduced reduction product solubility and improved stability with high voltage cathodes.^[44] Motivated by the high energy density found in Li metal battery chemistry, stabilizing these electrolytes for Li metal anodes was of interest. It was found that using a highly fluorinated ether greatly improved the Li metal deposition and stabilized these electrolytes on Li metal anodes.^[15-18] This new class of electrolytes was classified as localized high-concentration electrolytes (LHCE). The name came from the concept that the addition of the fluorinated ether did not significantly change the solvation of the Li⁺ and it retained many of the unique properties found in highly concentrated electrolytes. Instead, the ether functioned as a diluent to isolate these locally concentrated solvation spheres. This had several benefits in addition to the improved Li metal performance including reducing the salt content (potential cost savings),

improving the viscosity and ionic conductivity, and allowing for the development of flame-retardant electrolytes that would normally provide performance issues in those conditions.

Motivated by this advancement in organic highly concentrated electrolytes, a search for a diluent that would function in aqueous-based electrolytes began. A direct transfer of the concept of taking the highly fluorinated ethers was unsuccessful. Due to the large fluorine content, these HFE compounds were highly hydrophobic and incompatible with purely aqueous electrolytes (which was one of the reasons for their incorporation into the 4V aqueous battery passivation layer developed by Yang et al.).^[13] However, with the development of the hybrid class of electrolytes, the organic phase was found to be able to allow for partial miscibility of the highly fluorinated ether compounds with the hybrid electrolytes.

3.2.2 Fluorinated Ether Diluent

Finding the right amount of ether is an important consideration. Too little and it will not function in the diluent role of isolating the solvation spheres and too much causes phase separation. Since the HTe-21 utilizes TEP as the organic phase, it made sense to model the dilution after the LiFSI in TEP/BTFE system that was found to also be flame-retardant.^[16] The optimized ratio used was a 1:3 molar ratio between TEP and BTFE. A variety of fluorinated compounds were tested including 2,2,2trifluoroethyl-1,1,2,2-tetrafluoroethyl ether (previously referred to as HFE) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TFEP), and fluorinated ether analogs 1,2-(1,1,2,2-tetrafluoroethoxy) ethane (TFEE), tris(2,2,2-trifluoroethyl) orthoformate (**Figure 27**). These were selected due to their availability, varying functionality, and previous use in ALIB systems. It was found that the 1:3 molar ratio happened to be the maximum amount of HFE and TFEP that was able to be added to HTe-21 and avoid phase any noticeable separation. In addition to those two ratios, HFE, TFEP, TFEE, and TFEO were also analyzed at a 1:1 molar ratio between the TEP and diluent, collectively referenced as HETe-2X1, where X is the molar ratio of the ether to the two solvents (**Table 1**).



Figure 27: Structures of various fluorinated ethers and ether analogues.

Table 1: Molar composition of HTe-21 +	- fluorinated ether diluent electrolytes.
--	---

		HETe-231					
	HFE	TFEP	TFEE	TFEO	HFE	TFEP	
LiTFSI		30.5%					
Water		18.6%					
TEP		9.3%					
Ether	17.4%				55.8%		
Diluted Concentration (mol/kg)	4.2m	3.9m	3.7m	3.3m	1.24m	1.09m	

Full cells were assembled and cycled in a similar manner as previously discussed. Initial investigation into the effect of the diluent structure indicated that aside from TFEO, all other fluorinated diluents performed similarly to the baseline HTe-21 (**Figure 28A**). The TFEO significantly hindered cycling indicating that orthoformates may not be ideal diluents in ALIBs. This may be due to the structure of

the orthoformate. If it were to begin to decompose with the loss of a fluorinated ethoxide functional group, it would form a carbocation that would be partially stabilized due to bulkiness and resonance structures, and delocalization of the positive charge to the neighboring oxygen atoms. This could further react with water leading to unwanted side reactions and it could explain the dramatic loss in performance. For the rest, there was no definitive indication of performance enhancement aside from being able to achieve slightly higher CE after many cycles. These first electrolytes were cycled at a low diluent content of a 1:1 molar ratio with the TEP. The next step was to increase to a 3:1 ratio to form the HETe-231 class of electrolytes to compare to the 3:1 ratio reported in the organic system.^[16] HFE was used as a model diluent since it displayed the highest CE of the tested diluents. Figure 28B shows that upon increasing the diluent content, performance begins to suffer. The performance also suffers upon increasing the cutoff potential to 2.80V (Figure 28C). Looking at the first cycle of the 2.80V cutoff cell, an additional inflection point just below 2.80V along with the long constant voltage charging phase suggests water decomposition leading to poor CE and loss of capacity (Figure 29).



Figure 28: (A) TNO vs. LMO full cells cycling at a C/3 rate with an upper voltage cutoff of 2.45V with various fluorinated diluents in the HETe-211 electrolyte. (B) Cycling results showing effect of increasing fluorinated diluent content using HFE as a representative sample. (C) C-TNO vs. LMO cells cycling at a C/3 rate with an upper voltage cutoff of 2.80V using HFE as a representative sample.



Figure 29: Charge/discharge profile of the first cycle for the 2.8V carbon coated TNO vs. LMO cell using HETe-211 (HFE). Arrow is included to highlight the additional inflection point in the charging curve.

Post cycling analysis was conducted through the use of X-ray photoelectron spectroscopy (XPS) on the TNO anodes to analyze the SEI. **Figure 30** shows how the pristine TNO electrode (green) compares to the cycled TNO electrodes after cycling at 2.80V in HTe-21 and HETe-211 (HFE) (red and blue, respectively). **Figure 30A,E** show characteristic signals from the Nb₂O₅ in the pristine TNO. These are benchmark signals that can be used to assess if an SEI has formed. Since the signal for both electrolytes shows the absence of these characteristic Nb peaks, it can be concluded that the surface has been effectively coated with a robust SEI. A more in-depth discussion of the SEI will be provided in the next section (**3.2.3 1,4-Dioxane Diluent**). **Figure 30A-D** shows that the SEI formed in the HTe-21 and HETe-211 (HFE) feature similar peak components due to all new peaks showing similar shapes. Also of importance in **Figure 30F** is the absence of any phosphorus-containing SEI component in contrast to what has been observed in TMP hybrid electrolytes.^[29] This can mean one of two things, either the phosphorus-containing components form first and are covered by non-phosphorus-containing components, or the TEP is more stable than the TMP and does not reduce to form SEI components at these working potentials. Based on the LSV shown in **Figure 22**, no TEP reduction peak is observed until after 1V vs. Li/Li⁺ in the HTe-21 sample, which is outside of the range of this cell which would be expected to operate between the limits of 1V-4.5V based on cell potential and analogous LMO/LTO systems previously published.^[29] With the high similarity between SEI components, it can be concluded that the fluorinated diluents do not participate in SEI formation at these potentials.



Figure 30: XPS results for pristine TNO electrode (green), cycled TNO in HTe-21 at 2.8V at a C/3 rate (red), and cycled TNO in HETe-211 (HFE) at 2.8V at a C/3 rate (blue) for binding energy ranges analyzing Li1s and Nb4s (A), F1s (B), O1s (C), C1s (D), Nb3d(E), and P2p (F). All samples were washed with DMC to remove trace solvent and vacuum dried prior to XPS analysis.

Further analysis of the bulk electrolyte properties using LSV, FTIR, and TCA indicate key changes in the electrolyte that would not benefit enhanced stability (**Figure 31**). The LSV of HTe-211 (HFE) (**Figure 31A**) shows a loss in both reductive and oxidative stability upon the addition of the HFE. FTIR analysis (**Figure 31B**) shows that the HFE effectively dilutes the electrolyte as there is no change in the water solvation structure upon the addition of the HFE without any additional salt. While the conductivity of the HETe-211 (HFE) is enhanced (**Figure 31C**) when compared to the HTe-21, it is only a minimal increase when compared to the WIS21 baseline conductivity. Additionally, a phase change is observed at lower temperatures not observed in the HTe-21 upon the forward scan (negative scan).



Figure 31: (A) LSV of HTe-21 (red) vs HETe-211 (HFE) (grey). (B) FTIR of WIS21 (green), HTe-21 (purple), and HETe-211 (HFE) (green). (C) TCA results showing change in HETe-211 (HFE) compared to the previously discussed electrolytes.

The evidence in the cycling data, XPS, LSV, FTIR, and TCA data all point to no significant benefit from the HFE. This is believed to be due to the highly hydrophobic and water immiscibility properties of the fluorinated diluents. It is possible that since the HFE is only miscible with the TEP portion, phase separation may occur leading to the loss of electrochemical stability seen in the LSV as the water is pushed out of the hybrid phase and behaves more similarly to the WIS21. This is also indicated by the phase change observed which is most likely the aqueous phase precipitating at lower temperatures as seen in the WIS21 curve. In order to adapt the diluent concept to aqueous systems, a water-miscible diluent (and water and organic miscible diluent for hybrids) needs to be used to prevent any phase instability and loss of performance.

3.2.3 1,4-Dioxane Diluent

Recent studies have identified the cyclic ether (1,4-dioxane) as a promising diluent in aqueous electrolytes.^[18-20] Due to its two oxygens being 2.8 Å apart, it fits into the H-bonds in water well (2.7-3.0 Å), providing relatively good hydrophilicity when compared to other cyclic ethers.^[45-47] However, upon reaching a critical amount of 1,4-dioxane in water, the bulk properties change from a homogeneous mixture to a heterogeneous mixture where water can become localized in pockets of the dioxane diluent. This presents an interesting idea that the addition of the dioxane would require a critical amount in order to dominate the bulk properties and create the LHCE environment. Validation of this idea was provided by Nian et al.^[20] when 1,4-dioxane was added to the WIS21 at a molar ratio of 1:1 water:dioxane yielded similar cycling performance to the base WIS21, but upon a 1:2 ratio, significant cycling improvements were found (**Figure 32**). With the replacement of WIS21 with HTe-21,





Figure 32: Discharge capacities and Coulombic efficiencies (CE) of LTO/LMO full cells. Reproduced with permission from [20]. Copyright 2021 American Chemical Society. (Copy of Figure 6 for quick reference)

TEP and 1,4-dioxane were also found to be miscible together and could be reasonably added to the HTe-21 without concerns of phase stability and create a new class of hybrid LHCE, referred to as HDTe-2X1 (X=molar ratio of 1,4-dioxane). In addition to its miscibility, 1,4-dioxane was also an appropriate diluent due to its low solubility towards LiTFSI (<0.25m at room temperature) and low volatility compared to the fluorinated ethers.^[48] One of the only issues with the use of 1,4-dioxane is safety. Not only is it highly flammable, but it also possesses health risks and requires removal from wastewater due to its high chemical stability.^[49] Due to its role as a diluent, even when mixed at low quantities with WIS21 or HTe-21, it maintains its flammability. A non-flammable alternative that is miscible has not been identified yet and dioxane has been used in this study to elucidate the benefits brought on by aqueous diluents.

While it has been made clear that there is a critical amount of dioxane required, it is unclear what indicates that threshold. Therefore, a range of diluent quantities was investigated to shed some light on any key molar ratios that provide optimal performance in the diluted WIS21 (referred to as HDO-1X where X is the molar ratio of dioxane) and in the HDTe-2X1 electrolytes (Table 2). The electrolytes were selected to maintain different dioxane ratios in the HDO-12 within the HDTe-2X1 system. The ratios held constant are highlighted in red.

 Table 2: Molar compositions of tested HDTe-2X1 electrolytes compared to the HDO-12 system showing which molar rations were held constant in red.

	Ratio	mol%					Dioxane Ratio					
Electrolyte		LiTFSI	Water	TEP	Solvent*	Electrolyte**	Dioxane	TEP	Water	Solvent	Electrolyte	Litfsi
HDO-12	Reference Electrolyte	11%	30%	0%	30%	41%	59%	0.00	2.00	2.00	1.45	5.29
HDTe-211	1:1 TEP:dioxane	31%	35%	17%	52%	83%	17%	1.00	0.50	0.33	0.21	0.57
HDTe-221	1:1 water:dioxane	26%	30%	15%	44%	70%	30%	2.00	1.00	0.67	0.42	1.14
HDTe-241	1:2 water:dioxane	20%	23%	11%	34%	54%	46%	4.00	2.00	1.33	0.84	2.27
HDTe-261	1:2 solvent:dioxane	16%	19%	9%	28%	44%	56%	6.00	3.00	2.00	1.26	3.41
HDTe-271	1:1.45 electrolyte:dioxane	15%	17%	9%	26%	40%	60%	7.00	3.50	2.33	1.47	3.98
HDTe-2931	1:5.29 LiTFSI:dioxane	13%	14%	7%	21%	34%	66%	9.30	4.65	3.10	1.95	5.29

*Solvent is the sum of the moles of TEP and moles of Water

**Electrolyte is the sum of the moles of LiTFSI and moles of solvent

As with the aqueous dioxane system, there appears to be key mol fraction regimes for the hybrid dioxane system. Cycling results in 2.45V TNO vs. LMO cells cycled at a CCCV rate of C/3 cluster into several different groups (**Figure 33**). The lowest dioxane content (HDTe-211, red plot) was hindered by the addition of the dioxane. While its CE eventually outperforms the HTe-21 (black plot), it is still unable to break the 99% CE and displays poorer discharge capacity. HDTe-221 (orange) and HDTe-241 (brown) provide improved performance over HTe-21 due to the improved CE (>99%, purple bracket), with increased dioxane content delivering slightly higher discharge capacity. The highest regime in terms of CE is highlighted with the red bracket. It includes electrolytes HDTe-261, HDTe-271, and HDTe-2931. All three deliver an excellent CE of >99.5%. Upon increasing the dioxane content from HDTe-261 to HDTe-271, the discharge capacity also improves; however, a further increase to HDTe-2931 yields no further improvement and potentially a decrease in capacity. This highlights the critical threshold of the dioxane content >55mol% dioxane and an optimized content when the total molar ratio of electrolyte:dioxane is fixed to 1:1.45.



Figure 33: TNO vs. LMO cycling results for HDTe-2X1 at a rate of C/3 and a cutoff potential of 2.45V showing the capacity (A) and coulombic efficiency (B).

One possible reason for this continued improvement can be observed in the conductivity measurements. **Figure 34** shows the effect of adding dioxane to WIS21

(blue) and HTe-21 (purple). What is interesting is the reversal of trends. Upon addition of dioxane to WIS21 to form HDO-12 (orange), there is a drop in conductivity but an increase in temperature stability. This makes sense as the viscosity of WIS21 is not so high that it significantly diminishes the electrolyte's conductivity but the dioxane does not readily contribute to the solvation and conduction of Li-ions. The enhanced temperature stability may arise from the disruption of solid formation and suppression of precipitation. On the other hand, the massive loss in conductivity in the hybrid is improved by nearly an order of magnitude (purple to dark green). When a moderate amount of dioxane is added (HDTe-241, light green), conductivity begins to recover but temperature instability remains. The optimized HDTe-271 (dark green) continues to receive a conductivity boost and displays the highest temperature stability of all the tested aqueous electrolytes with no phase change observed within the temperature range tested, even maintaining around 0.8 mS/cm at -10 °C, opening up possibilities of enhanced lowtemperature applications. This opposite trend compared to the aqueous system may be due to the dramatic improvement in viscosity outweighing the inability to conduct Liions by the dioxane.



Figure 34: TCA plot of dioxane containing electrolytes with conductivity trends highlighted with arrows.

The HDTe-271 shows a similar rate performance under the CCCV charging profile as the base HTe-21 (**Figure 35A**). When the cutoff potential is increased to 2.80V on an uncoated TNO anode, electrolyte decomposition leads to rapid cell failure (red curve) as indicated by the poor 1st cycle CE of 56%. With a carbon coated TNO anode (**Figure 35B**), the HDTe-271 (blue) can perform exceptionally well, even when compared to the organic LP57 (red). When compared to the HDO-12, the HDTe-271 performs better at both 2.45V (**Figure 35C**) and 2.80V (**Figure 35D**) cutoffs highlighting the benefit of the TEP component in improving cycling performance. **Figure 35E**,**F** analyzes the first two cycles for the data plotted in **Figure 35D** to illustrate the enhanced stability offered by the HDTe-271. On the first constant voltage charge for the HDO-12 (red), the cell charges higher without returning any additional discharge capacity indicating the presence of water

decomposition. This is further demonstrated in the dQ/dV plot where the HDO-12 (red) displays a small rise near 2.80V indicating the electrolyte decomposition which is further shown by the shift in intercalation peak for the second cycle (orange). Meanwhile, the HDTe-271 has a reasonably good first cycle CE of around 90% leading to low overpotential growth on the second cycle and good cycling performance.



Figure 35: (A) TNO vs LMO full cells cycling in HTe-21 and HDTe-271. Upper potential cutoff and charge rate are 2.45V and C/3, respectively, unless stated otherwise. (B) Carbon coated TNO vs LMO full cells cycling to 2.80V. Comparison of HDTe-271 and HDO-12 electrolytes in TNO vs. LMO full cells cycling at a rate of C/3 and a potential cutoff of 2.45V (C) and 2.80V (D). Charge/discharge (E) and dQ/dV (F) plots of the first two cycles of carbon coated TNO vs LMO full cells cycling at a rate of C/3 and a potential cutoff of 2.80V.

The LSV plots (Figure 36) show that the HDO-12 and HDTe-271 provide similar stabilities at low potentials seen in the TNO/LMO system (>1V). Figure 36B enlarges the lower voltage region to highlight an enhanced stability of the HDTe-271 (green) over the HDO-12 (purple) at the lowest potentials, and also demonstrates a change in behavior between the HDTe-241 (green dash) and HDTe-271 with the additional passivation plateau seen. Since the only difference between HDO-12 and HDTe-271 is the TEP, this plateau is attributed to TEP reduction and explains why no phosphorus-containing SEI component was observed in the HTe-21 XPS results. But what is more important for providing the improved cycling performance between the HDTe-271 and HDO-12 can be seen at high potentials. Literature has shown that the addition of 1,4-dioxane can lead to oxidative decomposition at high potentials.^[48] In the HDO-12, this leads to a loss of stability at higher potentials. Upon moderate amounts of dioxane in the HDTe-241, there appears to be a small increase in current around the Al corrosion potential but when increasing to HDTe-271, the Al corrosion current is further reduced once again demonstrating the importance of the hybrid electrolyte base over the aqueous electrolyte base.



Figure 36: (A) LSV of various electrolytes. Al working electrode, activated carbon counter electrode, Ag/AgCl reference electrode, and a scan rate of 0.5 mV/s. Inserts show enlarged low (B) and high (C) potential limits of the dioxane containing electrolytes.

Figure 37 shows the CV for HTe-21 and HDTe-271 with a scan rate of 0.5 mV/s using an Ag/AgCl reference electrode. CV results demonstrate that the TEP reduction at low potentials (**Figure 37B**) leads to electrode passivation opening the possibility for even higher voltage cells if suitable anode chemistries are found. Cycling at high potentials demonstrates the major issue of metal corrosion. In typical cells, Al and SS are the common metals used due to their low cost. However, even at potentials used by LMO, there are considerable corrosion issues with both materials in even the most stable electrolyte (**Figure 37D,E**). As expected, using Ti (**Figure 37F**) shows excellent cycling stability at higher potentials further supporting the belief that electrolyte instability with the metal cell components creates a significant barrier to improving ALIB cycle life.



Figure 37: CV scans used a metal foil working electrode, activated carbon counter electrode, and Ag/AgCl reference electrode at a scan rate of 0.5 mV/s. Low voltage scan of HTe-21 (A) and HDTe-271 (B). High voltage scan of HDTe-271 first cycle metal foil summary (C) and detailed first three cycles for SS (D), Al (E), and Ti (F).

After adding the dioxane, the overall chemistry of the SEI does not change significantly based on XPS analysis (**Figure 38**). There are some minor differences between electrolytes. HDO-12 (yellow) shows some slight peak shifts (**Figure 38A,C**) and ratio differences (**Figure 38D**) but overall is not showing any new chemistries. A more detailed analysis of the HDO-12 SEI has been previously reported in the literature^[20] and will not be further discussed here as no major differences were observed. The lack of a P peak in **Figure 38E** indicates no contribution to the SEI from the TEP phase as previously mentioned and similarities

between HDTe-21, HDO-12, and HDTe-2X1 indicate that the dioxane also does not significantly contribute to SEI formation. Figure 38F,G have very weak signals, but the presence of these signals indicates that the SEI is primarily a result of salt decomposition. However, even though the dioxane may not participate in SEI formation, it does appear to improve SEI stability. As previously mentioned, the use of diluents helps to improve the stability of reduction products. This is observed in the stability of the O1s signature for HDTe-271 (blue) seen in **Figure 38C**. This peak located around 528 eV is indicative of Li₂O. While this can be an important SEI component, it readily reacts with water and CO₂ to form LiOH and Li₂CO₃, respectively. The solubilities of LiOH and Li₂CO₃ are 12.8 g/100 mL and 1.29 g/100 mL in water. Compared to the well-known LiF SEI component's solubility of 0.134 g/100 mL, this is a 1 to 2 order of magnitude increased solubility. Due to the high dioxane content preventing water from reaching the surface, these SEI components are allowed to remain on the surface and provide a more robust protective layer. This higher Li₂O content can also be confirmed in Figure 38A with the larger Li1s signal showing a larger contribution at lower eV values resulting from the Li₂O contribution.



Figure 38: XPS spectra of cycled carbon coated TNO cells after cycling at a rate of C/3 with an upper cutoff potential of 2.80V using HTe-21 (green), HDO-12 (yellow), HDTe-241 (red), and HDTe-271 (blue). Elements of interest are shown including Li1s and Nb4s (A), C1s (B), O1s (C), F1s (D), P2p (E), N1s (F), and S2p (G).

Looking more closely at the XPS spectra for HDTe-271 (**Figure 39**), SEI components are largely composed of decomposition products from LiTFSI and dissolved atmospheric gases such as CO₂ and O₂ rather than from the organic components which would be expected to give more polymeric and phosphate-containing SEI components. Nevertheless, these results further support the existence of a robust and effective SEI. Peak fitting assignments clearly show the strong presence of Li₂O and the improved SEI performance for the HDTe-271 over other tested electrolytes.



Figure 39: Fitted XPS spectra for carbon coated TNO cycled at C/3 at a cutoff potential of 2.80V vs. LMO in HDTe-271 showing elemental signatures for Li1s (A), C1s (B), O1s (C), and F1s (D).

As already mentioned, there are distinct differences between cells cycled to a 2.45V cutoff and a 2.80V cutoff, and this was also observed in the XPS results in **Figure 40**. The blue (2.45V cutoff) and green (2.80V cutoff) curves represent cycled TNO samples from cells containing HDTe-271 but at different cutoff potentials. What is most obvious is that for the 2.45V cutoff, virtually no change from the pristine TNO (red) is observed, and little to no SEI products are seen. This is most readily observed in **Figure 40E** showing the clear and strong Nb peak for the Nb₂O₅ in the TNO anode. And no LiF or Li₂O is observed (**Figure 40A,C**). This indicates that the ability of the cell to cycle at a cutoff of 2.45V is due entirely to the increased stability

of the HDTe-271 electrolyte compared to the WIS21 while the ability to cycle at a cutoff of 2.80V is due to the increased stability and SEI forming ability.



Figure 40: XPS spectra of pristine carbon coated TNO (red), carbon coated TNO cycled in HDTe-271 with a C/3 rate and a cutoff potential of 2.45V (blue) and 2.80V (green). Elemental signatures are shown for L1s and Nb4s (A), C1s (B), O1s (C), F1s (D), and Nb3d (E).

While TEP does not appear to undergo reduction in this system to participate in SEI formation, it does appear to become oxidized and participate in a cathode electrolyte interphase (CEI) formation (**Figure 41A**). The presence of the Mn2p3 signature (**Figure 41B**) indicates that this is either not a complete coating or is less than 10 nm thick. In addition to TEP-based CEI components, species resulting from TFSI are observed from the N1s and S2p signatures (**Figure 41C,D**). This CEI phase may be one of the reasons for the improved high-voltage stability of the HDTe-271 and TEP-containing electrolytes when compared to the HDO-12 and WIS21 electrolytes.



Figure 41: XPS spectra of cycled LMO electrodes from HDTe-271 cells with a 2.45V (red) or 2.80V (blue) cutoff. Elemental signatures are shown for P2p (A), Mn2p3 (B), N1s (C), and S2p (D).

Since new SEI formation is not the reason for the enhanced performance of the HDTe-271 over HTe-21 and HDO-12, another underlying phenomenon must be responsible in addition to the improved SEI stability. As already mentioned with the FTIR analysis of WIS21 and HTe-21, changes in the solvation structure lead to some of the improvements of the highly concentrated 21m WIS when compared to lower concentrations such as 1m, 5m, or 10m WIS. Immediately upon inspection of the -OH stretching vibration for water, a major shift in peak shape occurs upon the addition of 1,4-dioxane (**Figure 42**). This is entirely due to the interaction between dioxane and water since dioxane does not have any IR bands in this region (**Figure 42C**, blue plot). In both the WIS21 and HTe-21 systems, as dioxane content is increased, the free -OH peak vanishes, and the H-bond peak associated with two anions begins to decrease with more and more dioxane. As those two peaks go down, the water Hbond peak with 1 anion and another molecule and the peak for H-bonds with 2 other solvent molecules both grow. In the pure WIS21 electrolyte, this was originally attributed to water-water H-bonds. In the dioxane electrolytes, this can now be attributed to increased interaction between water molecules and dioxane molecules and directly speaks to the dramatic change in the solvation structure previously discussed. Since one of the main factors for water decomposition in aqueous electrolytes is cation and anion-bound water being brought to the electrode surfaces, the ability of dioxane to interact with the water and change the solvation structure,^[20] less water decomposition occurs and less gas formation occurs disrupting SEI formation. This could potentially promote a thicker, more stable SEI for improved CE and cycle life.



Figure 42: (A) FTIR plot of changes to OH stretching vibration of WIS21 upon increasing amounts of dioxane.(B) FTIR plot of changes to OH stretching vibration of HTe-21 upon increasing amounts of dioxane. (C)Summary FTIR plot of changes from base WIS21 and HTe-21 electrolytes to optimized HDO-12 and HDTe-271 electrolytes.

The combination of improved viscosity, enhanced ESW, and solvation structure change all combine to dramatically enhance the battery performance of this new class of diluted hybrid electrolytes. Using a carbon coated TNO anode and LMO cathode, full cells were successfully cycled with a 2.8V cutoff potential achieving an initial discharge capacity of 187 mAh/g with a CE of 91.1%. After 40 cycles it retained 93.5% of its initial discharge capacity delivering 175 mAh/g with a CE of 99.3% and an even more impressive retention of 92.5% after 90 cycles with a capacity of 173 mAh/g and a CE of 99.5%. This is the highest capacity reported at this time for any ALIB without any sort of anode protection layer. This compares well with the same system using LP57. The HDTe-271 electrolyte provides 98.6% of the 1st cycle discharge capacity of the LP57 cell and still provides 93.4% of the 40th cycle discharge capacity of the LP57 cell. The biggest difference leading to the lost capacity is the much higher CE of the LP57 electrolyte, 95% after the first cycle and quickly rising to >99.9%. This loss of CE in ALIBs, to which metal corrosion is a contributing factor, needs to be addressed in order to make ALIBs competitive with organic LIBs. Another critical issue that needs to be addressed is the safety aspect of the dioxane diluent. While it provides considerable improvements, its toxicity and flammability are critical hurdles that need to be overcome with alternative chemistry if it is to be a reliable alternative.

Chapter 4: Anode Modifications

4.1 Anode Chemistry

4.1.1 LTO

Lithium titanium oxide (LTO, Li₄Ti₅O₁₂) is a very popular anode for ALIBs due to several reasons. First and foremost is that it is the only practical option for this voltage range. Due to it being readily commercially available, well characterized, and conveniently located right at the edge of the WIS21 ESW, it is an ideal anode for testing for improved stability of modified aqueous electrolytes. Also, thanks to its relatively flat charge/discharge plateau, it provides a very nice boundary for establishing stability and ensuring all available capacity is achieved (Figure 43A). When paired with LMO, a cycling cutoff potential between 2.7-2.8V is necessary to extract the maximum capacity (Figure 43B). When HTe-21 (brown) and WIS21 (purple) are cycled at 2.5V, only a small fraction of the capacity is retained and the poor CE on the WIS21 demonstrates the usefulness of LTO as a stability benchmark in ALIBs. As the cutoff for the HTe-21 is raised to 2.6V (green) and 2.7V (blue), the output capacity rises as expected. However, the CE also significantly drops between the 2.5V and 2.7V cells. This further demonstrates the challenge of using TEP as the co-solvent due to it not producing additional SEI components that allowed other systems using TMP, DMC, dioxane, etc., to fully cycle on LTO. While HTe-21 does show an extended ESW down to 1V vs. Li/Li⁺, that is on a blocking electrode and not representative of practical limitations including increased surface area and nucleation sites, and titanium oxide's ability to catalyze water reduction.^[50] Finding an

alternative anode that better utilizes the full ESW of more stable aqueous electrolytes is of great interest to advancing the ALIB field. Also, finding an anode that provides a more competitive capacity (LTO – 160 mAh/g vs. Graphite – 370 mAh/g) is key for raising the energy density.



Figure 43: (A) LTO half-cell in LP57 with a charging current of 20 μA. (B) LTO vs. LMO cells following a constant current rate change protocol. LP57 with a cutoff of 2.9V (red) marking maximum expected capacity. WIS21 with a cutoff of 2.5V (purple). HTe-21 with a cutoff of 2.5V (brown), 2.6V (green), and 2.7V (blue).

4.1.2 TNO

Titanium Niobate (TNO, TiNb₂O₇) has been increasingly investigated as an alternative anode to LTO, especially in regard to fast charge/discharge capabilities.^{[51,} ^{52]} It provides an intriguing alternative to LTO due to the decreased titanium content (10mol% vs. 20mol% in LTO), higher capacity (225 mAh/g vs. 160 mAh/g in LTO), and its sloped profile pushes the voltage down to 1V vs. Li/Li⁺, effectively improving the average discharge voltage of a full cell coupled with LMO (Figure 44A). Another interesting aspect of TNO is the ability to provide stable full cell performance with WIS21, something not possible with LTO. Even at 1.6V vs. Li/Li⁺, TNO can provide a possible 90 mAh/g prior to the LTO plateau, providing the possibility for full ESW utilization in the base WIS21 system if coupled with a high-voltage cathode. Figure **44B** demonstrates the ability of WIS21 to operate in a TNO/LMO cell with a 2.5V cutoff potential (orange), something not possible with LTO. Furthermore, the cutoff can be further increased to 2.6V (black) with only a minor decrease in observed CE. The performance with HTe-21 (Figure 44C) is a bit more challenging. While the HTe-21 can reach higher cutoff potentials (up to 2.8V, purple) with a similar CE as the 2.6V WIS21, it can reach much higher capacities. However, rate performance is a major issue when increasing from C/10 to 1C. This also speaks to why using LTO has been so popular, being commercially available, high-quality electrodes can be purchased, increasing reproducibility and reliability of cell cycling while TNO must be coated in-house, which can lead to wider variability between studies.

79



Figure 44: (A) TNO half-cell in LP57 with a charging current of 20 μA. (B) TNO vs. LMO cells following a constant current rate change protocol. LP57 half-cell with a cutoff of 2.9V (red) demonstrating maximum capacity. WIS21 with a cutoff of 2.5V (orange) and 2.6V (black). (C) HTe-21 with a cutoff of 2.5V (brown), 2.6V (green), 2.7V (blue), and 2.8V (purple).

One side effect of running cells at a higher rate is that the CE can be artificially enhanced due to not allowing the cell to remain at the unstable potentials as long as they would at a low rate. This effect can readily be seen in Figure 44B with the drop in CE observed for the initial C/10 cycles (cycles 1 and 2) compared to the 1C cycles (cycles 9-19). By switching to a CCCV protocol, a drop in CE is observed, even at similar rates; however, the protocol is able to minimize capacity loss from rate changes (Figure 45). In Figure 45A, the orange plot and blue plot are both using WIS21 at a cutoff of 2.5V. However, the orange plot uses a constant current protocol with a varying rate ranging from C/10 to 1C. The blue plot uses a CCCV protocol at a 1C rate. Between cycles 9-19, both cells are undergoing a 1C rate with the CCCV showing a lower CE but higher capacity. This discharge capacity is similar to the capacity at the lower rates in cycles 1-8 in the orange plot. A more dramatic capacity improvement is seen in Figure 45B due to the issues with high rates for the highly viscous HTe-21. While they are at slightly different cutoff potentials, the blue plot from Figure 45A and the black plot from Figure 45B are both using CCCV protocols at 1C and deliver similar capacities, but importantly, the CCCV clearly shows the stability improvement of the HTe-21 over the WIS21 with a lower CE.



Figure 45: Comparison of changing the charging protocol from a variable rate constant current method to a single rate CCCV method for WIS21 (A) and HTe-21 (B).

4.1.3 PNO (Titanium Free)

With the success of replacing LTO with TNO, it merited further investigation into finding an alternative that was Ti-free. Researchers at the US Army Research Laboratory have been actively investigating XNO anode chemistries through doping, coatings, and element replacement. One particular anode of interest completely replaced the Ti transition metal with the non-metal, P, providing the anode material phosphorus niobate (PNO). When comparing the half-cell profiles of the three anodes (Figure 46), both PNO and TNO provide additional capacity at lower voltages than LTO and offer more capacity are higher voltages where LTO is inactive. However, PNO is currently not competitive enough with TNO to fully replace it. In addition to providing less capacity (195 mAh/g), it also displays a significant capacity fade between the charge and discharge cycles indicating the material may be less stable than TNO. Nevertheless, PNO was employed in full cells to compare how it performed vs. TNO. Figure 47 shows the cycling performance of PNO vs. LMO full cells with HDTe-271 and a CCCV protocol at a C/3 rate compared to identical TNO cells. Most notably, at both cutoff potentials, PNO provides less capacity and demonstrates poor capacity retention which is not fully explained by the CE. This goes back to the loss of capacity observed in the half-cell and speaks to the instability of the anode material.



Figure 46: Half-cell plots of LTO (red), TNO (purple), and PNO (green) between 1V and 2.5V at a charging current of 20 μ A.



Figure 47: (A) PNO half-cell in LP57 with a charging current of 20 μA. (B) PNO and (C) TNO full cells with an LMO cathode and HDTe-271 electrolyte following a CCCV charging protocol at a rate of C/3 at a 2.45V (red) and 2.60V (green) cutoff potential.
All three electrodes can successfully cycle in ALIBs with varying degrees of performance. These results on pristine anodes are promising but indicate that there are still issues with electrolyte stability. A commonly used method for addressing surface-related issues is with anode surface coatings, both at the electrode and particle levels.

<u>4.2 Anode Coatings</u>

4.2.1 Grafting

Due to the issues of aqueous electrolytes with low voltage anodes and metal corrosion, an ideal passivation method would not only coat the particles, but all conductive surfaces to prevent electrolyte side reactions on all surfaces. Diazonium grafting is a powerful surface modification method.^[53-73] This method chemically attaches a functionalized aromatic carbon ring to almost any surface under the right conditions (Figure 48). It is versatile in that it can work in organic and aqueous media with almost any functionalized aryl amine precursor. The grafting undergoes a radical chain growth mechanism that self-terminates when electronic conductivity is lost with the surface. With control of various parameters, coating thickness can be reproducibly targeted. The actual grafting process is a redox reaction that can be initiated chemically with carbon, Cu, Fe, or another appropriate reducing agent, or it can be initiated electrochemically. Electrochemical methods have been shown to produce more uniform and thicker layers as well as grafting conducted in organic media. Additionally, using this method for battery applications has precedence based on several other studies looking to modify graphite^[59, 62, 65, 66] and LFP^[56] surfaces. In these works, the authors focused on grafting the individual particles prior to electrode fabrication. While this was sufficient for their method, it would not address the protection of other conducting surfaces such as conductive carbon and metal foil. Therefore, both electrochemical chemical coating methods were employed using acetonitrile as the solvent and reacting media, 0.1M LiTFSI as the electrolyte salt, 4x molar excess of isoamyl nitrite as the organic nitrite source for turning the aniline into the diazonium, and 0.1M of a functionalized aniline. For chemical grafting, no additional species were needed to initiate the reaction as the carbon in the graphite and conductive additive initiated the reactions. Chemical grafting occurred under constant stirring for at least 40 hours. Electrochemical grafting was conducted by holding the potential of the working electrode at -2V vs the counter electrode for 1 hour.



Figure 48: (A) Chemical reduction for aryl amines to form reactive diazonium intermediate. (B) Diazonium grafting mechanism. Reproduce with permission from [68].

A wide array of anilines were screened and a perfluorooctyl aniline (PFOAn) was selected due to having strong hydrophobic characteristics. After electrode modifications, a qualitative assessment of the effectiveness was conducted to see if the electrolyte would readily wet the surface or bead up, indicating a coated surface. If well coated, the electrolyte (whether aqueous-based or organic) would bead up on the surface indicating not only hydrophobic but omniphobic properties. To minimize uncoated metal in the cell, pouch cells were used so that all the metal on the anode side would be coated. However, coatings appeared to be ineffective at preventing electrolyte decomposition on coated LTO electrodes. While the surface was effectively modified as observed through changings in electrolyte wetting, cycling results showed no benefit (**Figure 49**). Based on this, it was assumed that the coating was either not uniform or ineffective at preventing the electrochemical reduction of water.



Figure 49: Cycling results of a coated LTO vs LMO pouch cell using WIS21 (blue) and a control LTO vs LMO cell (purple) with PFOAn structure shown.

4.2.2 Electrode Particle Coatings (Carbon, LATP, LiF)

It has been shown that various surface coatings on anodes can suppress the hydrogen evolution reaction (HER) in ALIBs.^[74] HER suppression is a critical aspect of improving first-cycle efficiencies and initial SEI formation. In addition to HER suppression, various surface coatings can provide benefits such as increased electronic conductivity (carbon coatings), hydrophobic characteristics (LATP), and SEI-like properties (LiF). These coatings have been applied to the active material particles prior to receiving them. The coated particles were then used for electrode fabrication with any coating masses taken into account to ensure the 80:10:10 ratio of active material:conductive carbon:PVDF binder was constant.

Due to the disappointing performance of PNO, this made an ideal testing ground for observing the benefits of coatings. Using an anode of 4wt% carbon coated PNO (C-PNO, 2% acetylene black, 2% carbon nanotubes), full cells were constructed using HDTe-271 and cycled to varying cutoff potentials vs LMO (**Figure 50**). As shown in **Figure 50A**, the carbon coating significantly improved the performance of the PNO anode at both 2.45V and 2.60V cutoff potentials. The overall CE improvement, especially on the first cycle, led to considerable improvements in terms of cycling stability, especially at 2.45V. Pushing the cutoff potential further, successful cycling was achieved as high as 2.80V (blue plot) prior to rapid failure at 2.90V (purple plot) (**Figure 50B**). A comparison of the C-PNO in an organic LP57 electrolyte (black plot) shows that even with the carbon coating, there are still stability issues that need to be addressed before the PNO anode can be realistically used as an alternative to TNO or even LTO.



Figure 50: (A) Comparison of PNO and C-PNO anodes using HDTe-271 at 2.45V and 2.60V cutoff potentials.(B) C-PNO full cells using HDTe-271 cycled to 2.45V (brown), 2.60V (green), 2.80V (blue), and 2.90V (purple) cutoff potentials and LP57 -cell reference (black).

For TNO, four different anode coatings were provided and tested (**Figure 51**). LATP (0.6wt%) (LATP-TNO), LiF (hydrothermally treated in a 4wt% solution) with a 4wt% carbon coating (2% acetylene black, 2% carbon nanotubes) (LiF-TNO), a specially developed nanoporous TNO grown on reduced graphene oxide (npC-TNO), and a 2wt% (acetylene black) carbon-coated TNO (C-TNO). Full cell TNO vs LMO cycling at C/3 using HDTe-271 at 2.45V (**Figure 51A**) and 2.60V (**Figure 51B**) cutoff potentials is shown. All coatings allowed for cycling at 2.45V with C-TNO (blue plot) demonstrating the best performance and the only coating to offer an improvement over the bare TNO (red plot). Furthermore, at 2.60V, only the C-TNO was able to achieve stable cycling, with the LiF-TNO undergoing catastrophic cell failure. Thanks to the HER suppression, less electrolyte is reacted at 2.45V prior to SEI formation. After SEI formation at 2.60V, the benefit of the HER suppression is seen even more clearly with a more robust SEI formed.



Figure 51: Cycling data for full cells with uncoated TNO (red), LATP coated TNO (orange), LiF-Carbon coated TNO (brown), nano-porous carbon coated TNO (green), and carbon coated TNO (blue) at 2.45V (A) and 2.60V (B) cutoff potentials with HDTe-271 electrolyte.

As previously discussed, TNO offers the unique advantage of allowing WIS21 to cycle at a lower cell cutoff potential of 2.45V, as shown in **Figure 52A**. With C-TNO (**Figure 52B**), performance is improved to allow for less than 10% capacity loss after 100 cycles at a high rate of 4C (purple plot). Results at C/10 (red plot) demonstrate that while the coating does help suppress the HER, it does not eliminate it and the suppression appears to have more of a kinetic benefit than purely an

electrochemical stability benefit. Without the carbon coating, the WIS21 has significant electrolyte decomposition even on a minor increase of cutoff potential to 2.5V (black plot). Using C-TNO, cells can cycle stably for nearly 40 cycles before CE decay indicates a failure problem. The use of C-TNO is a step forward in the direction of providing a wider range of cell chemistries depending on desired electrolyte properties. It allows for purely aqueous systems to provide moderate energy density for superior safety applications without sacrificing cost, conductivity, and rate capabilities, which are often required with WIS modifications.



Figure 52: WIS21 full cells with uncoated TNO (A) and carbon coated TNO (B) anodes. Effects of cycling rate and cutoff potential are shown.

Analysis of C-TNO in the best aqueous-based electrolyte (HDTe-271) yields the best-performing ALIB reported yet in terms of the combination of ESW, conductivity, viscosity, cell voltage with an LMO cathode, and specific capacity. **Figure 53** shows the impressive ability of the C-TNO vs LMO system to reach stable cycling at a 2.8V CCCV charging cutoff providing 187 mAh/g (CE=91.1%) first cycle capacity and retaining 92.5% after 90 cycles with a CE of over 99.5% at a rate of C/3. As shown by the LP57 cell in blue, C-TNO vs. LMO is extremely stable with only a 1% loss of capacity after 10 cycles at a slow C/10 rate. With only a 1% loss of capacity after 10 cycles at a slow C/10 rate. With only a 1% loss of capacity at 2.8V for LP57 (purple) after 16 cycles, the higher rate of decay for HDTe-271 (brown) again goes back to likely being a result of corrosion on the cathode side. If the CE of the HDTe-271 can be improved, it is already on par with LP57 based on the first cycle discharge capacity alone. **Figure 53B** shows the huge improvement offered by the carbon coating at 2.80V when the C-TNO (brown) is compared to the same system using uncoated TNO (black).



Figure 53: (A) HDTe-271 full cells with carbon coated anode at 2.45V (red), 2.60V (orange), 2.80V (brown), and 2.90V (green) cutoff potentials with LP57 shown for reference at 2.80V (purple) and at 3.0V (blue) cutoffs. (B) Comparison of benefit of carbon coating the TNO anode in identical HDTe-271 cells (coated – brown, uncoated – black).

With the optimized anode and cycling protocol used for all of the electrolyte classes, a tremendous improvement has been made over the base WIS21 electrolyte (**Figure 54**). Evolving from a pure aqueous electrolyte (red) to a hybrid electrolyte (green) was already a significant advancement for ALIBs, allowing for cycling in previously unreached systems. When further modifications are done to push the electrolyte with the addition of the 1,4-dioxane diluent, the crucial CE is improved to create a highly competitive aqueous-based electrolyte.



Figure 54: (A) 2.8V cutoff potential cycling summary of the studied electrolytes on in C-TNO vs LMO full cells.(B) CE for 2.8V electrolyte summary. (C) Enlargement of CE plot to highlight improvements.

Chapter 5: Summary and Future Directions

5.1 Project Summaries

5.1.1 Gel Polymer Electrolyte

This project demonstrated the ability to create a mechanically robust GPE to allow for the development of flexible ALIBs. Since the GPE was chemically crosslinked, it removed the need for an additional separator. The 3V system of LTO vs. LMO laid the foundation for the development of the GPE and allowed for the limits to be further pushed to develop the GPL and enable 4V flexible ALIBs. In addition to the practical engineering of the 4V GPE battery, TCA was conducted on a model GPE electrolyte to provide a deeper understanding of the changes that occur upon UV polymerization of GPEs at various monomer fractions. This result is significant in helping to better characterize and design future iterations of GPEs. Another key result of this project, specifically the 4V project, was the scale-up to industry. Proving that real batteries can be fabricated with this advanced system to solve real-world problems.

5.1.2 Electrolyte Modification

Following up on the groundbreaking advancements in the field of ALIB electrolyte design, a safer hybrid electrolyte was developed replacing flammable and/or toxic organic phases with a safer TEP solvent. Testing of the HTe-21 electrolyte helped to highlight some of the challenges facing ALIBs in the attempt to increase the cell voltage and overall energy density of the battery. While great work has been done to improve low potential stability, major issues with electrolyte stability both due to electrolyte decomposition and metal corrosion remain, as demonstrated through this research.

Continued innovation also led to the development of a new class of aqueousbased electrolytes in the development of a localized highly concentrated hybrid aqueous/non-aqueous electrolyte, combing the benefits of all three contributing liquid components. This work helped to highlight how adjusting the solvation structure of the electrolyte and reducing reductive product solubility can be as important if not more important than providing new SEI components. These results suggest that the current SEI formed by aqueous electrolytes may be sufficient and other issues need to be addressed such as HER suppression, solvation control, SEI stability, safety, ionic conductivity, and cathode issues.

5.1.3 Anode Modifications

Since the development of WIS, ALIBs have been primarily limited in pushing the limits by the lack of stable alternatives to LTO. This dissertation has demonstrated the first use of TNO in an aqueous electrolyte and demonstrated the ability to push the cell voltage beyond the previous 2.7V maximum with an LMO cathode. Coupling TNO with high-voltage cathodes like LNMO could potentially push ALIBs into 3.5V-4.0V ranges with higher anode-specific capacities of over 225 mAh/g, providing energy densities that would begin to compete with organic systems.

In order to truly compete with the LP57 cells, the CE of ALIBs must be improved. As demonstrated through the use of a simple carbon coating, significant CE increases can be achieved through the modification of the anode surface. Using C-TNO and HDTe-271, an impressive full cell system is shown, outputting over 185 mAh/g based on anode AM mass and a maximum cell voltage of 2.8V. Furthermore, with an impressive CE of >99.5%, stable cycling was observed up to 90 cycles with less than 8% capacity fade. Continued cycling is expected for many more cycles before the 80% capacity retention benchmark is expected to be hit.

5.2 Future Directions for Aqueous Lithium-Ion Batteries

The results of this dissertation shed light on several key areas that need to be addressed for the future of ALIBs if there is any hope for them to find a role in the currently dominated organic LIB market. Herein, I will discuss additional topics for research and possible experimental designs to begin to investigate them.

5.2.1 Protecting the Anode

While the diazonium grafting was unsuccessful in this work, further optimization and refinement of the grafting procedure can surely create a uniform and dense protective layer as has been demonstrated in other areas of diazonium grafting research. In assessing the effectiveness of the grafting, special care must also be given to the desired functionality of the surface and its ability to facilitate SEI growth and repair as well as compatibility with Li⁺ diffusion and electrolyte compatibility.

Optimization of the anode coatings can provide even further benefits for ALIBs. Even though the tested LiF-coated anode was not a success, incorporating more inorganic SEI components could be an effective way for preparing an SEI foundation and improving the first cycle CE. Previous studies^[74] reported that other coatings, such as Al₂O₃, may be even more effective at suppressing the HER and could further improve the electrolyte stability of low and high cutoff potentials.

5.2.2 Stabilizing the Electrolyte

Much work has been done to expand the ESW of aqueous-based electrolytes to the point that they are now in the range of Li-Al alloy and closing in on graphite potentials. However, electrolyte decomposition still does occur in working full cells. With the theoretical ESW well expanded, more work can be devoted to expanding the practical window of aqueous electrolytes. Particularly at higher voltages where corrosion is a major concern. Al and SS corrosion have been overlooked issues in the field of ALIBs. When using LMO, it has often been assumed that there is no issue with corrosion, and only when pushing the cathode chemistry to LNMO potentials do researchers address the issue by using Ti foil. The use of Ti foil currently is a killing blow to any high-voltage cathode from a cost perspective for industry. Further studies should be devoted to looking for additives that can stabilize aqueous electrolytes against Al and/or SS or find an alternative cheap metal that is compatible at high potentials. Alternatively, using a Li salt that is less corrosive toward Al than LiTFSI could be another possibility.

To verify the true performance capabilities of new anodes and electrolytes, testing cells with LMO on Al, SS, and Ti foil can help to demonstrate how stable these new systems are at low potentials. Part of the lower CE could very well be due to corrosion on the cathode side and simply replacing the Al foil and SS casings with a more stable metal might allow for the current TNO/LMO system to match the LP57 performance and reach 3V operating voltages.

As shown in the LSV of the HDTe-271, the TEP reduction at very low potentials may be a way to improve the SEI further with formation cycling. The cell potential can be pushed on the first cycle or two to allow for TEP reduction before it is reduced to the practical limit for the electrode chemistry to gain additional benefit from the TEP phase in the electrolyte.

5.2.3 Alternative Electrode Chemistries

While TNO has provided significant advances, there is the possibility that it may be contributing to premature electrolyte decomposition and limitation of the practical electrolyte ESW. Alternative niobate anodes should be explored in addition to PNO. Current literature searches suggest that the development of TNO and its derivates is an active field of research with studies looking into dopants, Ti replacement, and crystal structure modifications. With the ever-expanding ESW, looking to stabilize aqueous electrolytes with Li-Al alloy anodes or Si anodes could greatly improve the energy density of ALIBs. On the cathode side, finding more alternative cathodes with higher specific capacities can improve the pack-level energy density of ALIBs. Newer cathodes like lithium manganese iron phosphate (LMFP) could provide a moderate voltage cathode to replace LMO, and high voltage cathodes like lithium cobalt phosphate (LCP) can test the high voltage stability.

5.2.4 Cheaper/Safer Alternatives

Safety and cost concerns are some of the most, if not the most, important considerations to take in the development of ALIB electrolytes. Current state-of-theart aqueous-based electrolytes walk a fine line in this area. The incorporation of components such as 1,4-dioxane and TMP can pose serious health concerns in the event of improper disposal of batteries and electrolyte precursors. Environmental concerns are also important with the chemical stability of many of the components like the TFSI anion and 1,4-dioxane persisting for a long time if contamination occurs. 1,4-dioxane is even at times classified as a forever chemical due to the difficulty of removing it during water treatment processes. And on top of the health and environmental concerns, 1,4-dioxane turns the once non-flammable aqueous electrolyte into a highly flammable one. Due to the massive benefit offered by diluents, considerable research should be undertaken to find safer, non-flammable alternatives to 1,4-dioxane. A focus on the flammability issue should be of the utmost importance. Finding a fluorinated version of 1,4-dioxane or dioxane derivative might be one way to help with that, but care must be taken to ensure miscibility with water is not prevented as was a major issue demonstrated by the HFE diluent.

5.2.5 Concluding Remarks

It is my firm belief that aqueous secondary batteries will play a crucial role in our future due to the high safety and cost savings potentials. With everything from our cars to our socks using rechargeable batteries, aqueous electrolytes have never been more needed. After 2015, the field of ALIBs took off with novel uses of WIS. Recently, research has begun to slow with many of the limitations of currently available systems being met and no suitable alternatives available to fall into the region of usability for aqueous-based electrolytes. I hope that the conclusions from my dissertation can help to reignite advancement in ALIBs. Through highlighting the overlooked high voltage corrosion to demonstrating a new class of diluent hybrid electrolyte and anode chemistry, I believe there are significant advances to be made in the near future to allow for the development and industry acceptance of a competitive ALIB for a wide variety of applications.

Bibliography

- FACT SHEET: President Biden Announces Steps to Drive American Leadership Forward on Clean Cars and Trucks. The White House: 2021.
- [2] New-Vehicle Prices Increase for Fifth Straight Month, Set Record Again in August, According to Kelley Blue Book. Kelley Blue Book: 2022.
- [3] Yoshino, A. The Birth of the Lithium-Ion Battery. *Angew. Chem. Int. Ed.* 2012, 51 (24), 5798-5800. DOI: 10.1002/anie.201105006.
- [4] Winter, M.; Barnett, B.; Xu, K. Before Li Ion Batteries. *Chem Rev* 2018, *118* (23), 11433-11456. DOI: 10.1021/acs.chemrev.8b00422.
- [5] Armand, M. A., P.; Bresser, D.; Copley, M.; Edström, K.;Ekberg, C.;
 Guyomard, D.; Lestriez, B.; Novák, P.; Petranikova, M.; Porcher, W.;
 Trabesinger, S.; Wohlfahrt-Mehrens, W.; Zhang, H. Lithium-ion batteries Current state of the art and anticipated developments. *Journal of Power Sources*2020, 479. DOI: 10.1016/j.jpowsour.2020.228708.
- [6] Tian, Y.; Zeng, G.; Rutt, A.; Shi, T.; Kim, H.; Wang, J.; Koettgen, J.; Sun, Y.;
 Ouyang, B.; Chen, T.; et al. Promises and Challenges of Next-Generation
 "Beyond Li-ion" Batteries for Electric Vehicles and Grid Decarbonization. *Chemical Reviews* 2021, *121* (3), 1623-1669. DOI:
 10.1021/acs.chemrev.0c00767.
- [7] Li, W.; Dahn, J. R.; Wainwright, D. S. Rechargeable lithium batteries with aqueous electrolytes. *Science* 1994, *264* (5162), 1115-1118. DOI: 10.1126/science.264.5162.1115.

- [8] Wang, Y.; Yi, J.; Xia, Y. Recent Progress in Aqueous Lithium-Ion Batteries. *Advanced Energy Materials* 2012, 2 (7), 830-840. DOI: https://doi.org/10.1002/aenm.201200065.
- [9] Heiskanen, S. K.; Kim, J.; Lucht, B. L. Generation and Evolution of the Solid Electrolyte Interphase of Lithium-Ion Batteries. *Joule* 2019, *3* (10), 2322-2333.
 DOI: https://doi.org/10.1016/j.joule.2019.08.018.
- [10] Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* 2015, *350* (6263), 938-943. DOI: 10.1126/science.aab1595.
- [11] Suo, L.; Borodin, O.; Sun, W.; Fan, X.; Yang, C.; Wang, F.; Gao, T.; Ma, Z.;
 Schroeder, M.; von Cresce, A.; et al. Advanced High-Voltage Aqueous
 Lithium-Ion Battery Enabled by "Water-in-Bisalt" Electrolyte. *Angew Chem Int Ed Engl* 2016, 55 (25), 7136-7141. DOI: 10.1002/anie.201602397.
- [12] Yamada, Y.; Usui, K.; Sodeyama, K.; Ko, S.; Tateyama, Y.; Yamada, A.
 Hydrate-melt electrolytes for high-energy-density aqueous batteries. *Nature Energy* 2016, 1 (10). DOI: 10.1038/nenergy.2016.129.
- [13] Yang, C.; Chen, J.; Qing, T.; Fan, X.; Sun, W.; von Cresce, A.; Ding, M. S.;
 Borodin, O.; Vatamanu, J.; Schroeder, M. A.; et al. 4.0 V Aqueous Li-Ion
 Batteries. *Joule* 2017, 1 (1), 122-132. DOI: 10.1016/j.joule.2017.08.009.
- [14] Wang, F.; Borodin, O.; Ding, M. S.; Gobet, M.; Vatamanu, J.; Fan, X.; Gao, T.;Eidson, N.; Liang, Y.; Sun, W.; et al. Hybrid Aqueous/Non-aqueous Electrolyte

for Safe and High-Energy Li-Ion Batteries. *Joule* **2018**, *2* (5), 927-937. DOI: 10.1016/j.joule.2018.02.011.

- [15] Chen, S.; Zheng, J.; Mei, D.; Han, K. S.; Engelhard, M. H.; Zhao, W.; Xu, W.;
 Liu, J.; Zhang, J. G. High-Voltage Lithium-Metal Batteries Enabled by
 Localized High-Concentration Electrolytes. *Adv Mater* 2018, *30* (21),
 e1706102. DOI: 10.1002/adma.201706102.
- [16] Chen, S.; Zheng, J.; Yu, L.; Ren, X.; Engelhard, M. H.; Niu, C.; Lee, H.; Xu, W.; Xiao, J.; Liu, J.; et al. High-Efficiency Lithium Metal Batteries with Fire-Retardant Electrolytes. *Joule* 2018, *2* (8), 1548-1558. DOI: 10.1016/j.joule.2018.05.002.
- [17] Ren, X.; Chen, S.; Lee, H.; Mei, D.; Engelhard, M. H.; Burton, S. D.; Zhao, W.;
 Zheng, J.; Li, Q.; Ding, M. S.; et al. Localized High-Concentration Sulfone
 Electrolytes for High-Efficiency Lithium-Metal Batteries. *Chem* 2018, *4* (8), 1877-1892. DOI: 10.1016/j.chempr.2018.05.002.
- [18] Chen, S.; Nian, Q.; Zheng, L.; Xiong, B.-Q.; Wang, Z.; Shen, Y.; Ren, X. Highly reversible aqueous zinc metal batteries enabled by fluorinated interphases in localized high concentration electrolytes. *Journal of Materials Chemistry A* 2021, 9 (39), 22347-22352, 10.1039/D1TA06987J. DOI: 10.1039/D1TA06987J.
- [19] Feng, R.; Chi, X.; Qiu, Q.; Wu, J.; Huang, J.; Liu, J.; Liu, Y. Cyclic Ether– Water Hybrid Electrolyte-Guided Dendrite-Free Lamellar Zinc Deposition by Tuning the Solvation Structure for High-Performance Aqueous Zinc-Ion

Batteries. *ACS Applied Materials & Interfaces* **2021**, *13* (34), 40638-40647. DOI: 10.1021/acsami.1c11106.

- [20] Nian, Q.; Zhu, W.; Zheng, S.; Chen, S.; Xiong, B.-Q.; Wang, Z.; Wu, X.; Tao,
 Z.; Ren, X. An Overcrowded Water-Ion Solvation Structure for a Robust Anode
 Interphase in Aqueous Lithium-Ion Batteries. ACS Applied Materials &
 Interfaces 2021, 13 (43), 51048-51056. DOI: 10.1021/acsami.1c15742.
- [21] Cresce, A.; Xu, K. Aqueous lithium-ion batteries. *Carbon Energy* 2021, 3 (5),
 721-751. DOI: https://doi.org/10.1002/cey2.106.
- [22] Langevin, S. A.; Tan, B.; Freeman, A. W.; Gagnon, J. C.; Hoffman, C. M., Jr.; Logan, M. W.; Maranchi, J. P.; Gerasopoulos, K. UV-cured gel polymer electrolytes with improved stability for advanced aqueous Li-ion batteries. *Chem Commun (Camb)* 2019, *55* (87), 13085-13088. DOI: 10.1039/c9cc06207f.
- [23] Cresce, A.; Eidson, N.; Schroeder, M.; Ma, L.; Howarth, Y.; Yang, C.; Ho, J.;
 Dillon, R.; Ding, M.; Bassett, A.; et al. Gel electrolyte for a 4V flexible aqueous lithium-ion battery. *Journal of Power Sources* 2020, *469*, 228378. DOI: https://doi.org/10.1016/j.jpowsour.2020.228378.
- [24] Ding, M. S.; Cresce, A. V.; Eidson, N.; Xu, K. Polymer-Supported Aqueous Electrolytes for Lithium Ion Batteries 1. Application of a Thermoconductometric Method to a LiTFSI + H 2 O + PDA Electrolyte System. J. Electrochem. Soc 2022. DOI: https://doi.org/10.1149/1945-7111/aca051

- [25] Ding, M. S.; Cresce, A. V.; Eidson, N.; Xu, K. Polymer-Supported Aqueous Electrolytes for Lithium Ion Batteries 2. Conductivity Gain upon Polymerization and Double Glass Transition in LiTFSI+H2O+PDA Gels. Submitted in J. Electrochem. Soc 2022.
- [26] Mucci, V.; Vallo, C. Efficiency of 2,2-dimethoxy-2-phenylacetophenone for the photopolymerization of methacrylate monomers in thick sections. *Journal of Applied Polymer Science* 2012, *123* (1), 418-425, DOI: https://doi.org/10.1002/app.34473.
- [27] Pitzer, L.; Sandfort, F.; Strieth-Kalthoff, F.; Glorius, F. Intermolecular Radical Addition to Carbonyls Enabled by Visible Light Photoredox Initiated Hole Catalysis. *Journal of the American Chemical Society* 2017, *139* (39), 13652-13655. DOI: 10.1021/jacs.7b08086.
- [28] Tung, C.-Y. M.; Dynes, P. J. Relationship between viscoelastic properties and gelation in thermosetting systems. *Journal of Applied Polymer Science* 1982, *27* (2), 569-574, DOI: https://doi.org/10.1002/app.1982.070270220.
- [29] Li, Q.; Yang, C.; Zhang, J.; Ji, X.; Xu, J.; He, X.; Chen, L.; Hou, S.; Uddin, J.; Addison, D.; et al. Controlling Intermolecular Interaction and Interphase Chemistry Enabled Sustainable Water-tolerance LiMn2O4||Li4Ti5O12 Batteries. *Angewandte Chemie International Edition* 2022, DOI: https://doi.org/10.1002/anie.202214126.
- [30] Fan, X.; Chen, L.; Borodin, O.; Ji, X.; Chen, J.; Hou, S.; Deng, T.; Zheng, J.;Yang, C.; Liou, S.-C.; et al. Non-flammable electrolyte enables Li-metal

batteries with aggressive cathode chemistries. *Nature Nanotechnology* **2018**, *13* (8), 715-722. DOI: 10.1038/s41565-018-0183-2.

- [31] Chen, J.; Vatamanu, J.; Xing, L.; Borodin, O.; Chen, H.; Guan, X.; Liu, X.; Xu, K.; Li, W. Improving Electrochemical Stability and Low-Temperature Performance with Water/Acetonitrile Hybrid Electrolytes. *Advanced Energy Materials* 2019, 1902654. DOI: 10.1002/aenm.201902654.
- [32] Dou, Q.; Lei, S.; Wang, D.-W.; Zhang, Q.; Xiao, D.; Guo, H.; Wang, A.; Yang, H.; Li, Y.; Shi, S.; et al. Safe and high-rate supercapacitors based on an "acetonitrile/water in salt" hybrid electrolyte. *Energy & Environmental Science* 2018, *11* (11), 3212-3219, DOI: 10.1039/C8EE01040D.
- [33] Cheng, X.; Yuan, J.; Hu, J.; Chen, S.; Yan, H.; Yang, W.; Li, W.; Dai, Y. 2.5 V High-Performance Aqueous and Semi-Solid-State Symmetric Supercapacitors Enabled by 3 m Sulfolane-Saturated Aqueous Electrolytes. *Energy Technology* 2022, *10* (6), 2200157, DOI: https://doi.org/10.1002/ente.202200157.
- [34] Ma, Z.; Chen, J.; Vatamanu, J.; Borodin, O.; Bedrov, D.; Zhou, X.; Zhang, W.;
 Li, W.; Xu, K.; Xing, L. Expanding the low-temperature and high-voltage limits of aqueous lithium-ion battery. *Energy Storage Materials* 2022, *45*, 903-910.
 DOI: https://doi.org/10.1016/j.ensm.2021.12.045.
- [35] Xie, J.; Liang, Z.; Lu, Y.-C. Molecular crowding electrolytes for high-voltage aqueous batteries. *Nature Materials* 2020, *19* (9), 1006-1011. DOI: 10.1038/s41563-020-0667-y.
- [36] Xu, J.; Ji, X.; Zhang, J.; Yang, C.; Wang, P.; Liu, S.; Ludwig, K.; Chen, F.;Kofinas, P.; Wang, C. Aqueous electrolyte design for super-stable 2.5 V

LiMn2O4 || Li4Ti5O12 pouch cells. *Nature Energy* **2022**, *7* (2), 186-193. DOI: 10.1038/s41560-021-00977-5.

- [37] Zeng, G.; Xiong, S.; Qian, Y.; Ci, L.; Feng, J. Non-Flammable Phosphate Electrolyte with High Salt-to-Solvent Ratios for Safe Potassium-Ion Battery. *Journal of The Electrochemical Society* 2019, *166* (6), A1217. DOI: 10.1149/2.1171906jes.
- [38] Xu, K.; Ding, M. S.; Zhang, S.; Allen, J. L.; Jow, T. R. Evaluation of Fluorinated Alkyl Phosphates as Flame Retardants in Electrolytes for Li-Ion Batteries: I. Physical and Electrochemical Properties. *Journal of The Electrochemical Society* 2003, *150* (2), A161. DOI: 10.1149/1.1533040.
- [39] Xu, K.; Ding, M. S.; Zhang, S.; Allen, J. L.; Jow, T. R. An Attempt to Formulate Nonflammable Lithium Ion Electrolytes with Alkyl Phosphates and Phosphazenes. *Journal of The Electrochemical Society* 2002, *149* (5), A622.
 DOI: 10.1149/1.1467946.
- [40] Xu, K.; Zhang, S.; Allen, J. L.; Jow, T. R. Nonflammable Electrolytes for Li-Ion Batteries Based on a Fluorinated Phosphate. *Journal of The Electrochemical Society* 2002, *149* (8), A1079. DOI: 10.1149/1.1490356.
- [41] Wang, X.; Yasukawa, E.; Kasuya, S. Nonflammable Trimethyl Phosphate Solvent-Containing Electrolytes for Lithium-Ion Batteries: I. Fundamental Properties. *Journal of The Electrochemical Society* 2001, *148* (10), A1058.
 DOI: 10.1149/1.1397773.
- [42] Wang, X.; Yasukawa, E.; Kasuya, S. Nonflammable Trimethyl Phosphate Solvent-Containing Electrolytes for Lithium-Ion Batteries: II. The Use of an

Amorphous Carbon Anode. *Journal of The Electrochemical Society* **2001**, *148* (10), A1066. DOI: 10.1149/1.1397774.

- [43] Zhang, Y.; Lewis, N. H. C.; Mars, J.; Wan, G.; Weadock, N. J.; Takacs, C. J.; Lukatskaya, M. R.; Steinrück, H.-G.; Toney, M. F.; Tokmakoff, A.; et al. Water-in-Salt LiTFSI Aqueous Electrolytes. 1. Liquid Structure from Combined Molecular Dynamics Simulation and Experimental Studies. *The Journal of Physical Chemistry B* 2021, *125* (17), 4501-4513. DOI: 10.1021/acs.jpcb.1c02189.
- [44] Alvarado, J.; Schroeder, M. A.; Zhang, M.; Borodin, O.; Gobrogge, E.; Olguin, M.; Ding, M. S.; Gobet, M.; Greenbaum, S.; Meng, Y. S.; et al. A carbonate-free, sulfone-based electrolyte for high-voltage Li-ion batteries. *Materials Today* 2018, *21* (4), 341-353. DOI: https://doi.org/10.1016/j.mattod.2018.02.005.
- [45] Harris, T. K.; Mildvan, A. S. High-Precision Measurement of Hydrogen Bond Lengths in Proteins by Nuclear Magnetic Resonance Methods. *Proteins: Structure, Function, and Bioinformatics* 1999, *35* (3), 275-282, DOI: https://doi.org/10.1002/(SICI)1097-0134(19990515)35:3<275::AID-PROT1>3.0.CO;2-V.
- [46] Takamuku, T.; Nakamizo, A.; Tabata, M.; Yoshida, K.; Yamaguchi, T.; Otomo, T. Large-angle X-ray scattering, small-angle neutron scattering, and NMR relaxation studies on mixing states of 1,4-dioxane-water, 1,3-dioxane-water, and tetrahydrofuran-water mixtures. *Journal of Molecular Liquids* 2003, *103-104*, 143-159. DOI: https://doi.org/10.1016/S0167-7322(02)00133-2.

- [47] Bakulin, I.; Kondratyuk, N.; Lankin, A.; Norman, G. Properties of aqueous 1,4-dioxane solution via molecular dynamics. *The Journal of Chemical Physics* 2021, *155* (15), 154501. DOI: 10.1063/5.0059337.
- [48] De Clercq, J.; Van de Steene, E.; Verbeken, K.; Verhaege, M. Electrochemical oxidation of 1,4-dioxane at boron-doped diamond electrode. *Journal of Chemical Technology & Biotechnology* 2010, 85 (8), 1162-1167, DOI: https://doi.org/10.1002/jctb.2415.
- [49] Choi, J. Y.; Lee, Y.-J.; Shin, J.; Yang, J.-W. Anodic oxidation of 1,4-dioxane on boron-doped diamond electrodes for wastewater treatment. *Journal of Hazardous Materials* 2010, *179* (1), 762-768. DOI: https://doi.org/10.1016/j.jhazmat.2010.03.067.
- [50] Zhang, X.; Zhang, B.; Huang, D.; Yuan, H.; Wang, M.; Shen, Y. TiO2 nanotubes modified with electrochemically reduced graphene oxide for photoelectrochemical water splitting. *Carbon* 2014, *80*, 591-598. DOI: https://doi.org/10.1016/j.carbon.2014.09.002.
- [51] Aghamohammadi, H.; Hassanzadeh, N.; Eslami-Farsani, R. A comprehensive review study on pure titanium niobium oxide as the anode material for Li-ion batteries. *Journal of Alloys and Compounds* 2022, *911*, 165117. DOI: https://doi.org/10.1016/j.jallcom.2022.165117.
- [52] Wen, X.; Ma, C.; Du, C.; Liu, J.; Zhang, X.; Qu, D.; Tang, Z. Enhanced electrochemical properties of vanadium-doped titanium niobate as a new anode material for lithium-ion batteries. *Electrochimica Acta* 2015, *186*, 58-63. DOI: 10.1016/j.electacta.2015.10.158.

- [53] Moock, D. S.; Steinmuller, S. O.; Wessely, I. D.; Llevot, A.; Bitterer, B.; Meier, M. A. R.; Brase, S.; Ehrenberg, H.; Scheiba, F. Surface Functionalization of Silicon, HOPG, and Graphite Electrodes: Toward an Artificial Solid Electrolyte Interface. *ACS Appl Mater Interfaces* 2018, *10* (28), 24172-24180. DOI: 10.1021/acsami.8b04877.
- [54] Menanteau, T.; Dias, M.; Levillain, E.; Downard, A. J.; Breton, T.
 Electrografting via Diazonium Chemistry: The Key Role of the Aryl Substituent in the Layer Growth Mechanism. *The Journal of Physical Chemistry C* 2016, *120* (8), 4423-4429. DOI: 10.1021/acs.jpcc.5b12565.
- [55] Assresahegn, B. D.; Brousse, T.; Bélanger, D. Advances on the use of diazonium chemistry for functionalization of materials used in energy storage systems. *Carbon* 2015, *92*, 362-381. DOI: 10.1016/j.carbon.2015.05.030.
- [56] Delaporte, N.; Perea, A.; Amin, R.; Zaghib, K.; Bélanger, D. Chemically grafted carbon-coated LiFePO4 using diazonium chemistry. *Journal of Power Sources* 2015, 280, 246-255. DOI: 10.1016/j.jpowsour.2015.01.014.
- [57] Yang, S.; Pan, Q.; Liu, J. Improving the cycleability of Si anodes by covalently grafting with 4-carboxyphenyl groups. *Electrochemistry Communications* 2010, *12* (3), 479-482. DOI: 10.1016/j.elecom.2010.01.024.
- [58] Martin, C.; Alias, M.; Christien, F.; Crosnier, O.; Bélanger, D.; Brousse, T.
 Graphite-Grafted Silicon Nanocomposite as a Negative Electrode for Lithium-Ion Batteries. *Advanced Materials* 2009, *21* (46), 4735-4741. DOI: 10.1002/adma.200900235.

- [59] Pan, Q.; Jiang, Y. Effect of covalently bonded polysiloxane multilayers on the electrochemical behavior of graphite electrode in lithium ion batteries. *Journal of Power Sources* 2008, *178* (1), 379-386. DOI: 10.1016/j.jpowsour.2007.12.025.
- [60] Abiman, P.; Wildgoos, G. G.; Compton, R. G. Investigating the Mechanism for the Covalent Chemical Modification of Multiwalled Carbon Nanotubes Using Aryl Diazonium Salts. *International Journal of Electrochemical Science* 2008, 3, 104-117.
- [61] Barrière, F.; Downard, A. J. Covalent modification of graphitic carbon substrates by non-electrochemical methods. *Journal of Solid State Electrochemistry* 2008, *12* (10), 1231-1244. DOI: 10.1007/s10008-008-0526-2.
- [62] Pan, Q.; Wang, M.; Chen, W. Hydrophobization of Metal Surfaces by Covalent Grafting of Aromatic Layer via Aryldiazonium Chemistry and Their Application in the Fabrication of Superhydrophobic Surfaces. *Chemistry Letters* 2007, 36 (11), 1312-1313. DOI: 10.1246/cl.2007.1312.
- [63] Mevellec, V.; Roussel, S.; Tessier, L.; Chancolon, J.; Mayne-L'Hermite, M.; Deniau, G.; Viel, P.; Palacin, S. Grafting Polymers on Surfaces: A New Powerful and Versatile Diazonium Salt-Based One-Step Process in Aqueous Media. *Chemical Materials* 2007, *19*, 6323-6330.
- [64] Chamoulaud, G.; Belanger, D. Spontaneous Derivatization of a Cu Electrode with in situ Generated Diazonium Cations in Aprotic and Aqueous Media. *Journal of Physical Chemistry C* 2007, 111, 7501-7507.

- [65] Pan, Q.; Wang, H.; Jiang, Y. Natural graphite modified with nitrophenyl multilayers as anode materials for lithium ion batteries. *J. Mater. Chem.* 2007, *17* (4), 329-334. DOI: 10.1039/b612422d.
- [66] Pan, Q.; Wang, H.; Jiang, Y. Covalent modification of natural graphite with lithium benzoate multilayers via diazonium chemistry and their application in lithium ion batteries. *Electrochemistry Communications* 2007, 9 (4), 754-760.
 DOI: 10.1016/j.elecom.2006.11.013.
- [67] Adenier, A.; Barré, N.; Cabet-Deliry, E.; Chaussé, A.; Griveau, S.; Mercier, F.;
 Pinson, J.; Vautrin-Ul, C. Study of the spontaneous formation of organic layers on carbon and metal surfaces from diazonium salts. *Surface Science* 2006, 600 (21), 4801-4812. DOI: 10.1016/j.susc.2006.07.061.
- [68] Pinson, J.; Podvorica, F. Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts. *Chem Soc Rev* 2005, 34 (5), 429-439. DOI: 10.1039/b406228k.
- [69] Combellas, C.; CDelamar, M.; Kanoufi, F.; Pinson, J.; Podvorica, F. I. Spontaneous Grafting of Iron Surfaces by Reduction of Aryldiazonium Salts in Acidic or Neutral Aqueous Solution. Application to the Protection of Iron against Corrosion. *Chemical Materials* 2005, 17, 3968-3975.
- [70] D'Amours, M.; Belanger, D. Stability of Substitued Phenyl Groups
 Electrochemically Grafted at Carbon Electrode Surface. *Journal of Physical Chemistry B* 2003, *107*, 4811-4817.
- [71] Kariuki, J. K.; McDermott, M. T. Nucleation and Growth of Functionalized Aryl Films on Graphite Electrodes. *Langmuir* 1999, 15, 6534-6540.

- [72] Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.;
 Saveant, J.-M. Covalent Modification of Carbon Surfaces by Aryl Radicals
 Generated from the Electrochemical Reduction of Diazonium Salts. *Journal of the American Chemical Society* 1997, *119*, 201-207.
- [73] Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J.-M. Covalent Modification of Carbon Surfaces by Grafting of Functionalized Aryl Radicals Produced form Electrochemical Reduction of Diazonium Salts. *Journal of the American Chemical Society* 1992, *114*, 5883-5884.
- [74] Wang, F.; Lin, C.-F.; Ji, X.; Rubloff, G. W.; Wang, C. Suppression of hydrogen evolution at catalytic surfaces in aqueous lithium ion batteries. *Journal of Materials Chemistry A* 2020, 8 (30), 14921-14926, DOI: 10.1039/D0TA05568A.

Publications and Presentations

Published

- [1] Ding, M. S.; Cresce, A. V.; Eidson, N.; Xu, K. Polymer-Supported Aqueous Electrolytes for Lithium Ion Batteries 1. Application of a Thermoconductometric Method to a LiTFSI + H 2 O + PDA Electrolyte System. *J. Electrochem. Soc* 2022. DOI: https://doi.org/10.1149/1945-7111/aca051
- [2] Eidson, N. & Cresce, A.; Schroeder, M.; Ma, L.; Howarth, Y.; Yang, C.; Ho, J.;
 Dillon, R.; Ding, M.; Bassett, A.; Stanzione, J.; Tom, R.; Soundappan, T.;
 Wang, C.; Xu, K., Gel electrolyte for a 4V flexible aqueous lithium-ion battery.
 Journal of Power Sources 2020, 469, 228378.
- [3] Liu, S.; Ji, X.; Piao, N.; Chen, J.; Eidson, N.; Xu, J.; Wang, P.; Chen, L.; Zhang, J.; Deng, T.; Hou, S.; Jin, T.; Wan, H.; Li, J.; Tu, J.; Wang, C., Inorganic-rich Solid Electrolyte Interphase for Advanced Lithium Metal Batteries in Carbonate Electrolytes. *Angew Chemie Int Ed* 2020, 60 (7), 3661-3671.
- [4] Long, C.; Cao, L.; Ji, X.; Hou, S.; Li, Q.; Chen, J.; Yang, C.; Eidson, N.; Wang,
 C., Enabling safe aqueous lithium ion open batteries by suppressing oxygen
 reduction reaction. *Nature Communications* 2020, 11 (1), 1-8.
- [5] Cui, C.; Yang, C.; Eidson, N.; Chen, J.; Han, F.; Chen, L.; Luo, C.; Wang, P.;
 Fan, X.; Wang, C., A Highly Reversible, Dendrite-Free Lithium Metal Anode
 Enabled by a Lithium-Fluoride-Enriched Interphase. *Adv Mater* 2020, 30 (12), 1906427.
- [6] Zhang, J.; Cui, C.; Wang, P.; Li, Q.; Chen, L.; Han, F.; Jin, T.; Liu, S.;
 Choudhary, H.; Raghavan, S. R.; Eidson, N.; Cresce, A. V.; Ma, L.; Uddin, J.;
 Addison, D.; Yang, C.; Wang, C., "Water-in-salt" polymer electrolyte for Li-ion batteries. *Energy & Environmental Science* 2020, 13 (9), 2878-2887.

- [7] Luo, C.; Ji, X.; Hou, S.; Eidson, N.; Fan, X.; Liang, Y.; Deng, T.; Jiang, J.;
 Wang, C., Azo Compounds Derived from Electrochemical Reduction of Nitro Compounds for High Performance Li-Ion Batteries. *Adv Mater* 2018, 30 (23), e1706498.
- [8] Wang, F.; Borodin, O.; Ding, M. S.; Gobet, M.; Vatamanu, J.; Fan, X.; Gao, T.;
 Eidson, N.; Liang, Y.; Sun, W.; Greenbaum, S.; Xu, K.; Wang, C., Hybrid
 Aqueous/Non-aqueous Electrolyte for Safe and High-Energy Li-Ion Batteries.
 Joule 2018, 2 (5), 927-937.
- [9] Gao, T.; Hou, S.; Huynh, K.; Wang, F.; Eidson, N.; Fan, X.; Han, F.; Luo, C.; Mao, M.; Li, X.; Wang, C., Existence of Solid Electrolyte Interphase in Mg Batteries: Mg/S Chemistry as an Example. *ACS Appl Mater Interfaces* 2018, 10 (17), 14767-14776.
- [10] Deng, T.; Fan, X.; Luo, C.; Chen, J.; Chen, L.; Hou, S.; Eidson, N.; Zhou, X.;
 Wang, C., Self-Templated Formation of P2-type K0.6CoO2 Microspheres for
 High Reversible Potassium-Ion Batteries. *Nano Lett* 2018, 18 (2), 1522-1529.
- [11] Li, X.; Gao, T.; Han, F.; Ma, Z.; Fan, X.; Hou, S.; Eidson, N.; Li, W.; Wang, C., Reducing Mg Anode Overpotential via Ion Conductive Surface Layer Formation by Iodine Additive. *Advanced Energy Materials* 2018, 8 (7), 1701728.
- [12] Yang, C.; Chen, J.; Qing, T.; Fan, X.; Sun, W.; Cresce, A. V.; Ding, M. S.;
 Borodin, O.; Vatamanu, J.; Schroeder, M. A.; Eidson, N.; Wang, C.; Xu, K.,
 4.0 V Aqueous Li-Ion Batteries. *Joule* 2017, 1 (1), 122-132.
- [13] Sun, W.; Suo, L.; Wang, F.; Eidson, N.; Yang, C.; Han, F.; Ma, Z.; Gao, T.;
 Zhu, M.; Wang, C., "Water-in-Salt" electrolyte enabled LiMn2O4/TiS2
 Lithium-ion batteries. *Electrochemistry Communications* 2017, 82, 71-74.

Submitted

- [1] Ding, M. S.; Cresce, A. V.; Eidson, N.; Xu, K. Polymer-Supported Aqueous Electrolytes for Lithium Ion Batteries 2. Conductivity Gain upon Polymerization and Double Glass Transition in LiTFSI+H2O+PDA Gels. *Submitted in J. Electrochem. Soc* 02-Sep-2022.
- [2] Cao, L.; Soto, F.; Li, D.; Deng, T.; Hu, E.; Cullen, D.; Lu, X.; Zachman, M.;
 Eidson, N.; Yang, X.; He, K.; Balbuena, P. B.; Wang, C., Pd-Ru pair on Pt surface for promoting hydrogen oxidation in alkaline media. *Submitted in Nature Communication*. 18-Aug-2022.

Plan to Submit

 Eidson, N.; Cresce, A.; Allen, J.; Ding, M.; Lewis, C.; Sun, H.; Xu, K.; Wang, C., Diluent Hybrid Aqueous/Non-Aqueous Electrolyte System Using TNO Anode. January 2023.

Invention Disclosures

 Cresce, A.; Eidson, N.; Wang, C.; Kang, X., Aqueous and Hybrid Aqueous/Non-Aqueous Gel Electrolytes. *Invention Disclosure*. University of Maryland and The U.S. Army Research Laboratory 2019.

Conference Presentations Delivered

- [1] Cresce, A. V. (presenter); Eidson, N.; Schroeder, M.; Ma, L.; Ding, M.; Xu, K., Gel Electrolytes for Lithium-Ion Batteries: An In-Situ Approach. 240th ECS Meeting, Digital, October 10-14, 2021.
- [2] Cresce, A. (presenter); Eidson, N.; Schroeder, M.; Ma, L.; Howarth, Y.; Yang,
 C.; Ho, J.; Dillon, R.; Ding, M.; Bassett, A.; Stanzione, J.; Tom, R.; Soundappan,
 T.; Wang, C.; Xu, K., Constructing a 4 Volt Aqueous Lithium Ion Battery Using
Acrylate-Based Gel Electrolytes. *PRiME 2020 (ECS, ECSJ, & KECS Joint Meeting)*, Digital, October 4-9, **2020**.

- [3] Cresce, A. V. (presenter); Eidson, N.; Xu, K.; Lundgren, C., Paradigm-Breaking Non-Flammable Lithium-Ion Batteries for Next-Generation Transportation Needs. *19th Annual Advanced Automotive Battery Conference 2019*, San Diego, CA, June 24-27, 2019.
- [4] Cresce, A. V. (presenter); Eidson, N.; Xu, K. C., Highly Concentrated Aqueous Gel Electrolytes for Diverse Battery Applications. 235th Meeting of The Electrochemical Society 2019, Dallas, TX, May 26-30, 2019.
- [5] Cresce, A. V. (presenter); Eidson, N.; Yang, C.; Wang, F.; Wang, C.; Xu, K., Separator-Free Gel Electrolytes Based on Water-in-Salt Solutions. *233rd Meeting of the Electrochemical Society 2018*, Seattle, WA, Poster Session, May 13-17, 2018.