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An Additive Study for Water-in-Salt Electrolyte (WiSE) with Lithium Manganese Oxide (LMO) and Titanium Niobate (TNO) Electrodes

by Jackson Carter, Matthew Sieh, Janet Sun, Brett Sweeney, Arthur von Cresce, Glenn Pastel, and Marshall A Schroeder

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14. ABSTRACT Aqueous electrolytes are poised to eliminate numerous safety concerns relative to state-of-the-art organic electrolytes; however, they continue to suffer from parasitic side reactions that consume lithium and limit performance. In this study we performed additive screening of 10 species for water-in-salt electrolytes (WiSEs) with the goal of forming a more robust and resilient anode solid-electrolyte interphase against hydrogen evolution at the anode. Coin cells consisted of a high-loading LiMnO ₂ cathode (13.32 mg cm ⁻²) and a low-loading TiNb ₂ O ₇ anode (3.32 mg cm ⁻²) to isolate the impact on anode performance. Down-selections were performed over the course of four experiments including 1) solubility, 2) impedance, 3) cycling retention, and 4) storage, with the baseline WiSE electrolyte outperforming all other WiSE-plus-additive compositions. However, the baseline WiSE electrolyte also suffered a 37% drop in energy density relative to similar cells with conventional organic electrolyte (1.0 M LiPF ₆ in ethylene carbonate:diethyl carbonate [EC:DEC]). Storage tests proved particularly useful for determining the amount of parasitic current at certain cell potentials (2.3, 2.4, and 2.5 V), which correlates to coulombic inefficiency. These results indicate a pressing need to reduce parasitic reactions at the anode by <u>investigating protective coatings and less-catalytic anode materials.</u>					
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1. Introduction

Aqueous batteries provide the opportunity for safer batteries and can be produced with ease due to the abundance of water on planet Earth.¹ With the recent advancements in the field, improvements in aqueous batteries could enable their commercialization in the future.² The baseline aqueous electrolyte consists of a highly concentrated solution of 20.0-molality (m) lithium (Li) bis(trifluoromethanesulfonyl) imide (LiTFSI) dissolved in water, known as a “water-in-salt” electrolyte (WiSE).³ However, challenges with aqueous batteries persist and are manifested in low capacity and low voltage compared to commercially available cells with standard organic electrolyte. The purpose of this study was to examine and analyze the impact of various additives on the WiSE with lithium manganese oxide (LMO) and titanium niobate (TNO) electrodes. LMO is a readily available commercialized cathode that lacks expensive transition metal cations such as cobalt and nickel. TNO is a newly developed anode capable of high charging rates and is being developed in parallel with other US Army Combat Capabilities Development Command Army Research Laboratory efforts. Electrolyte additives can help greatly improve the overall performance and can be critical to forming stable interphases. Ten additives were considered in this comparative study and evaluated based on solubility, impedance, cycling retention, and storage performance. All results were benchmarked against two controls: 1) 20.0-m LiTFSI in water as a WiSE control, and 2) an organic 1.0-molarity (M) lithium hexafluorophosphate (LiPF₆) electrolyte in ethylene carbonate (EC):diethyl carbonate (DEC).¹ By comparing the additive data to the controls, we can evaluate the impact of each additive on the electrode interphases and cycling stability.

2. Experimental Methods

Electrolyte Mixing. The baseline electrolyte consists of 20.0-m LiTFSI in ultrapure H₂O (>18 MΩ.cm, Millipore). To determine the solubility limit of each additive, increments of 1 wt% were added to 3 g of the baseline WiSE solution followed by sonication for 30 min and storage at 50 °C overnight. The baseline organic electrolyte consists of 1.0-M LiPF₆ in EC:DEC (3:7 weight ratio) without further optimization in a glovebox environment (Gotion).

Electrode Fabrication. The LMO cathode was graciously provided by the Argonne National Laboratory’s Cell Analysis, Modeling, and Prototyping facility. The cathode consisted of 90% LMO, 5% PVDF (polyvinylidene fluoride) binder, and 5% carbon nanotubes. The TNO anode, made in-house, is composed of 86% active material, 7% binder, and 7% conductive carbon. The anode mixture was cast

on aluminum-foil current collectors (CCs) with a 400- μm doctor blade height and dried overnight in a 50 °C oven. Individual electrode disks with 12-mm diameters were punched from both electrodes and weighed on a digital balance to obtain the average loading.

Cell Assembly. CR2032 coin cells with two electrodes, one separator, two spacers, and one spring were constructed for electrochemical tests. Cells containing the baseline organic electrolyte (1.0-M LiPF_6 in EC:EMC [3:7 ratio]) were constructed using stainless steel components inside an argon-filled glovebox (<0.1 ppm O_2 and H_2O). Cells containing the WiSE-based electrolytes were constructed outside of the glovebox on a laboratory benchtop in open-air conditions. When possible, aluminum-foil linings or aluminum-coated components were used to prevent electrolyte-induced corrosion of the stainless steel components. All cells used quartz-paper separators with a 1.6-cm diameter and contained a spacer–spring–spacer arrangement to maintain constant pressure across the entire surface area of the electrodes.

Electrochemical Impedance Spectroscopy (EIS). The EIS data was taken on a Biologic SP150 at room temperature. The AC perturbation signal was ± 10 mV, and the frequency ranged from 100 kHz to 100 mHz.

Galvanostatic Cycling. Cycling and storage tests took place on either a Neware or Maccor System at 30 °C. For both tests, cells underwent activation for two cycles between 1.5 and 2.6 V at a constant rate of C/5 (0.1 mA) followed by 10 cycles at 1C within the same voltage window (0.5 mA).

Storage tests were performed at 30 °C on activated full cells with variable upper cutoff potentials (UCVs) and a consistent 1.5-V lower cutoff potential. After activation, cells were charged using constant current protocol to the UCV, followed by a constant voltage protocol with a 5- μA cutoff current and storage under open-circuit conditions.

3. Results and Discussion

Additives were selected based on reports in the literature as well as suspected interphase formation mechanisms suitable for WiSE electrolytes (Table 1). Solubility testing revealed two species that were insoluble in the baseline WiSE solution at 1 wt% and were excluded from subsequent experiments. The remaining mixtures were tested at 1 or 5 wt% based on the solubility of the species with the exception of Lithion and poly(ethylene glycol), or PEG, which were tested at higher concentrations.

Table 1 List of the chemical species applied as an additive to the baseline WiSE solution

Chemical name	Supplier	Chemical formula	Suspected mechanism	wt%	Solubility
Acesulfame potassium salt	Sigma-Aldrich	$C_4H_4KNO_4S$	K^+ cation adsorption ⁴	1	Yes
Betaine	Alfa Aesar	$C_5H_{11}NO_2$	Hydrogen evolution inhibition ⁵	5	Yes
Calcium TFSI	Alfa Aesar	$Ca(C_2F_6NO_4S_2)_2$	TFSI reduction ²	1	Yes
Magnesium TFSI	TCI	$Mg(C_2F_6NO_4S_2)_2$	TFSI reduction ²	5	Yes
Vinylphosphonic acid	Sigma-Aldrich	$C_2H_5O_3P$	Electrochemical polymerization ⁶	1	Yes
Aquivion in H_2O	Sigma-Aldrich	$(C_4HF_7O_4S \cdot C_2F_4)_n$	Ion transport ⁷	N/A	No
Lithion in H_2O	Ion Power	$Li+C_nF_{(2n+1)}SO_3H+H_2O$	Oxidation stabilization ⁸	10	Yes
Benzene 1,4-diboronic acid	Sigma-Aldrich	$C_6H_8B_2O_4$	TFSI reduction ⁹	N/A	No
Ninhydrin	Sigma-Aldrich	$C_9H_6O_4$	TFSI reduction	5	Yes
PEG	Sigma-Aldrich	$C_{2n}H_{4n+2}O_{n+1}$	Cross-linking polymer density ¹⁰	20	Yes

Duplicate coin cells were constructed for each subsequent additive mixture with 100 μ L of electrolyte per cell. EIS tests before and after activation (Figs. 1a and 1b, respectively) help reveal the impact of the additive on solid-electrolyte interphase formation. In particular, extrapolating the right-most x-intercept of the first semi-circle in the EIS spectra represents the charge transfer resistance of the solid-electrolyte interphase (SEI). For all the cells, the charge transfer resistance after activation increased. For the baseline organic electrolyte, the charge transfer resistance increases from around 70 to 95 $\Omega \text{ cm}^{-2}$, a relatively modest increase that implies formation of a thin SEI. The WiSE-based electrolytes generated a much larger increase in charge transfer impedance, almost double pre-activation, indicating a much thicker or more resistive interphase. Notably, the interphases formed in the cells with ninhydrin and PEG at 20 wt% approach 150 $\Omega \text{ cm}^{-2}$. This fivefold increase suggests an interphase may have formed that is thick enough to significantly hinder Li-ion transfer between the electrolyte and electrodes. This prediction is validated by the poor cycling performance of these cells.

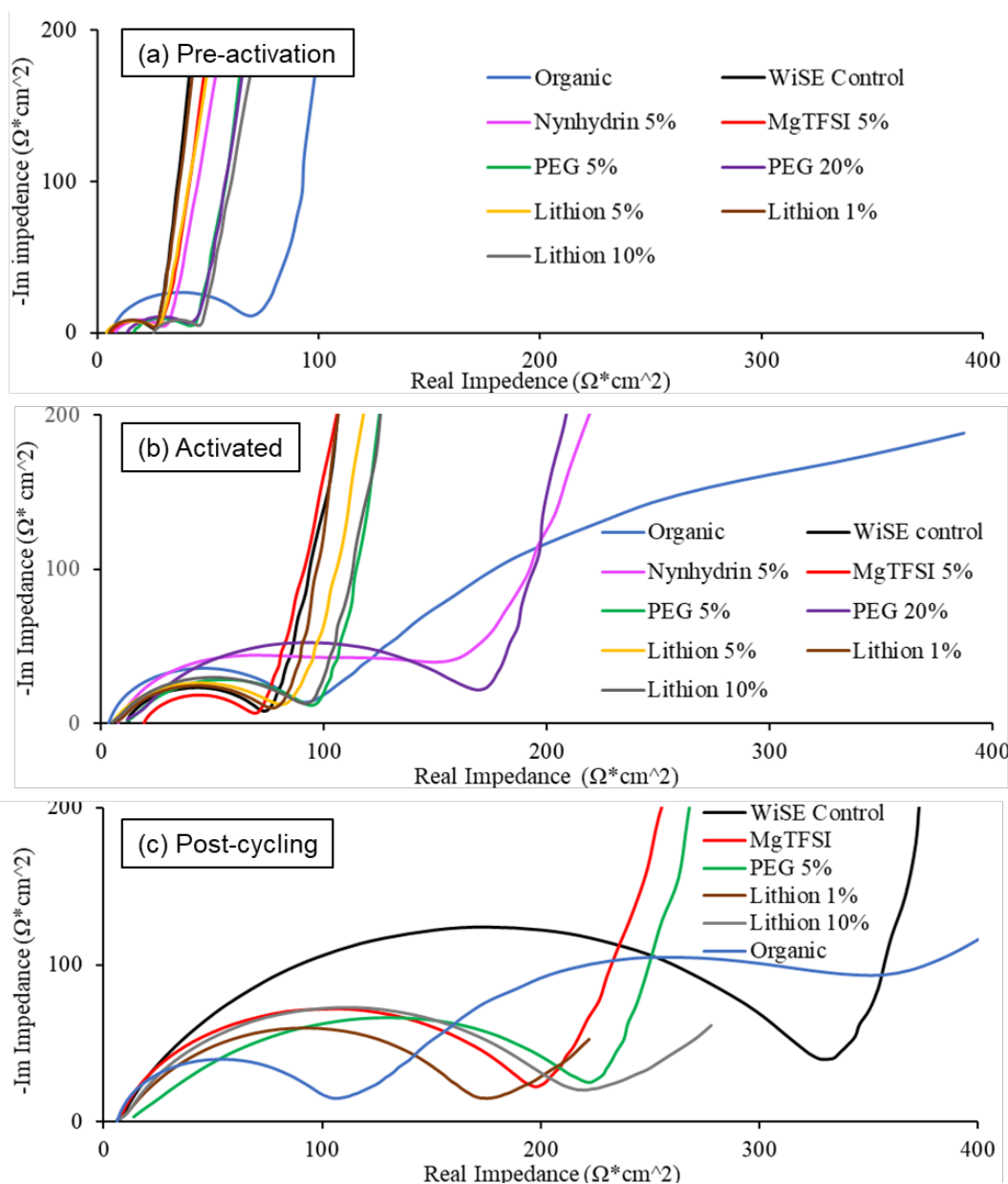


Fig. 1 EIS: (a) impedance pre-activation cycle, (b) impedance post-activation cycle, and (c) impedance after 10 charge–discharge cycles at constant current. Cells with particularly poor performance on activation were not cycled.

In Fig. 1c, the increase in impedance after cycling varies considerably between the electrolytes. While the impedance of the baseline organic electrolyte increases only slightly from around 95 to 105 $\Omega \text{ cm}^{-2}$, the baseline WiSE electrolyte exceeds 300 $\Omega \text{ cm}^{-2}$ —greater than any of the other additive-based compositions. Additive compositions that performed better than the WiSE baseline in order of lowest impedance include Lithion 1%, Mg(TFSI)₂, PEG 5%, and Lithion 10%. It is highly desirable to maintain a low and constant impedance, or the DC resistance, during operation of full cells. A gradual increase in impedance can often be a symptom of

many undesirable reactions, but it also represents an increase in overpotential that will complicate management of state-of-health and loss of energy. Therefore, the more limited increase in impedance for the additive-based cells is an immense benefit, although the cause is unknown. To better understand how these impedance measurements correlate with performance, we discuss the results from constant current cycling measurements.

The cycling data shown in Figs. 2a and 2b indicates that the baseline organic electrolyte produces significantly higher capacity initially and after 10 cycles. The cells containing the control WiSE electrolyte mixture were the next-best system, with a 28% drop in capacity relative to the organic control. This loss of capacity is seemingly associated with incomplete multistep reduction of Nb^{5+} to Nb^{3+} , processes that occur at a lower relative Li/Li^+ potential than Ti^{4+} to Ti^{3+} reduction. The later insertion/de-insertion process is unaffected, as seen by the similar capacity extracted between 2.2 and 1.5 V, suggesting incomplete lithiation of the anode material potentially due to parasitic reactions. Figure 2c helps reveal that the coulombic efficiency of the WiSE-based cells is poor ($<98\%$), with the baseline system performing the best. These low coulombic efficiency values represent a barrier to commercialization and deserve further investigation to determine the source(s) of irreversibility. The contrast in performance between the baseline organic and WiSE electrolytes emphasizes the need to improve SEI formation and prevent parasitic reactions.

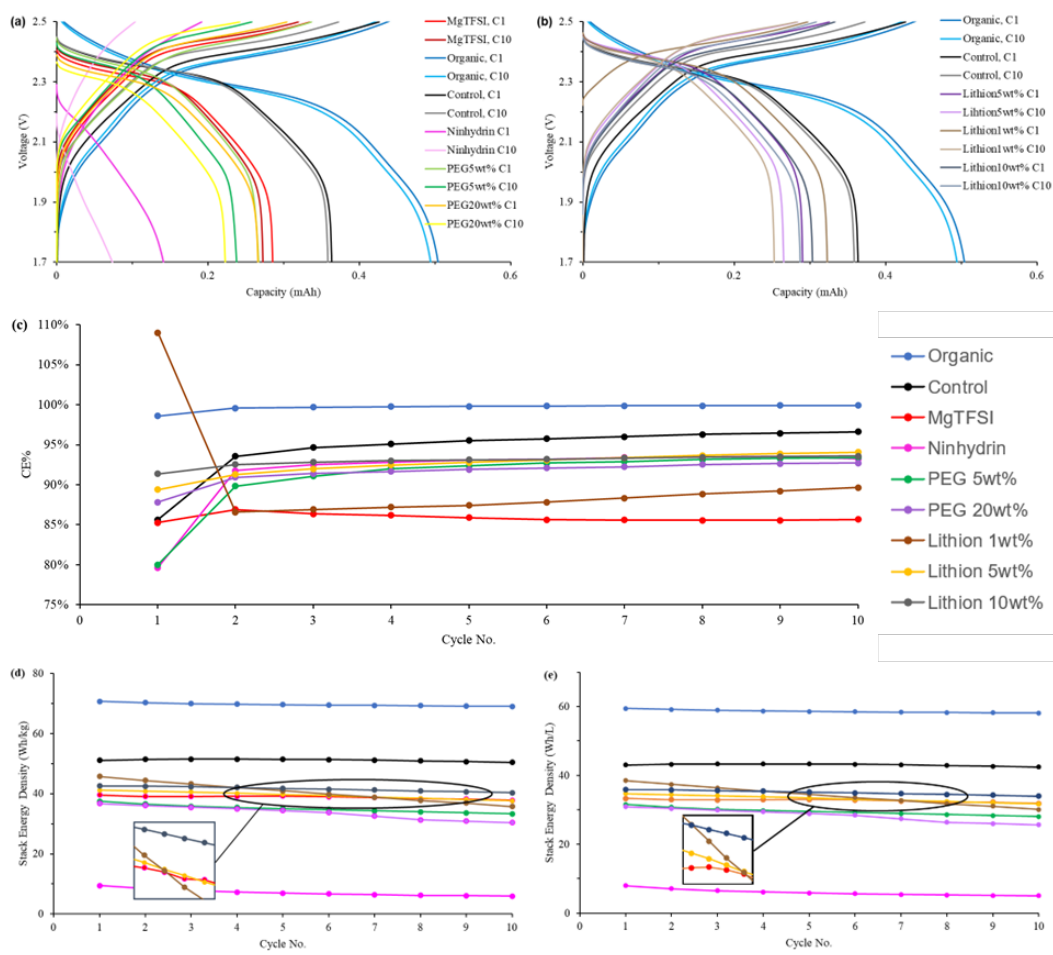


Fig. 2 Constant current cycling of the cells: (a) and (b) voltage vs. capacity for all cells after 1 cycle and 10 cycles, respectively; (c) coulombic efficiency over 10 cycles; and (d) and (e) stack energy densities with respect to active mass and active volume across 10 cycles, respectively. Note that the stack energy densities include the current collector and an incorrect averaging of the charge energy rather than the discharge energy.

Notably, the additive compositions that performed well in impedance tests, such as Lithion 1% and Mg(TFSI)₂, generated the worst coulombic efficiency of the cells cycled, with middling capacity and energy. This result hints at greater overall reactivity due to the addition of either species, with undesirable consequences. Similar to the rest of the additives in this study, although the impedance of the cells is improved over the baseline WiSE, the capacity and energy are negatively impacted.

There are several potential mechanisms behind the overall poor additive performances. The additive-influenced interphases may be too thick, which would greatly reduce the amount of diffusion possible among the Li-ions required to conduct charge and would be in line with the changes observed in the EIS data. Alternatively, the interphases may be insufficient to suppress parasitic hydrogen

evolution reactions (HERs) or may even be increasing them and therefore increasing the rate of cell degradation while also hindering Li-ion transport through the bulk electrolyte. One particular factor that may cause issues is wettability, as the aqueous electrolyte mixtures may be of such high viscosity that they would be incapable of properly wetting the electrodes through the chosen separator. While this study was not able to discern the exact mechanism behind the poor performances of the additive-electrolyte mixtures, cell deconstruction tests and further spectroscopy and microscopy analyses are recommended to obtain a more complete understanding of the inner workings of the cell.

While storage tests were not conducted on the cells containing the additive mixtures, data was still collected on the performance of aqueous cells with varying amounts of electrolyte compared with that of an organic cell with equivalent parameters. In Fig. 3, though the organic cell undergoes a very short constant-voltage step in Stage II and minimal voltage loss over the duration of Stage III, all of the WiSE cells exhibit a significantly longer constant-voltage stage followed by significant voltage loss at OCV (open-circuit voltage). This is due to the parasitic reactions that occur within the aqueous cell, represented by the non-negligible current present during the constant-voltage stage of the WiSE cells (10 μ A or C/50 at 2.6 V). The parasitic current can result in various detrimental effects, such as electrolyte consumption, cell component damage, and degradation of the anode interphase. A second round of tests was conducted to examine whether the UCV affected the degree of parasitic reactions, in which the cells were activated, cycled, and then set for storage tests at progressively lower voltage levels, the results of which are visible in Fig. 4.¹¹

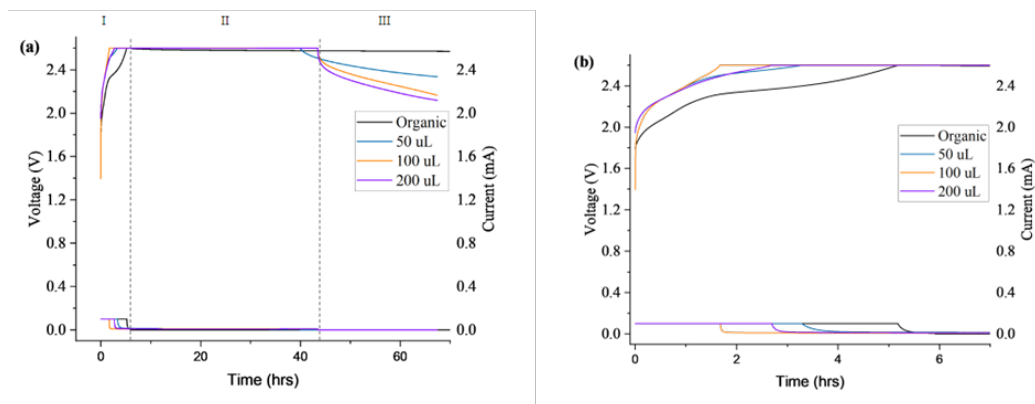


Fig. 3 Storage test at 2.6 V with various electrolyte amounts: (a) shows the storage test over the full period, and (b) shows only Phase I, the constant current charge phase

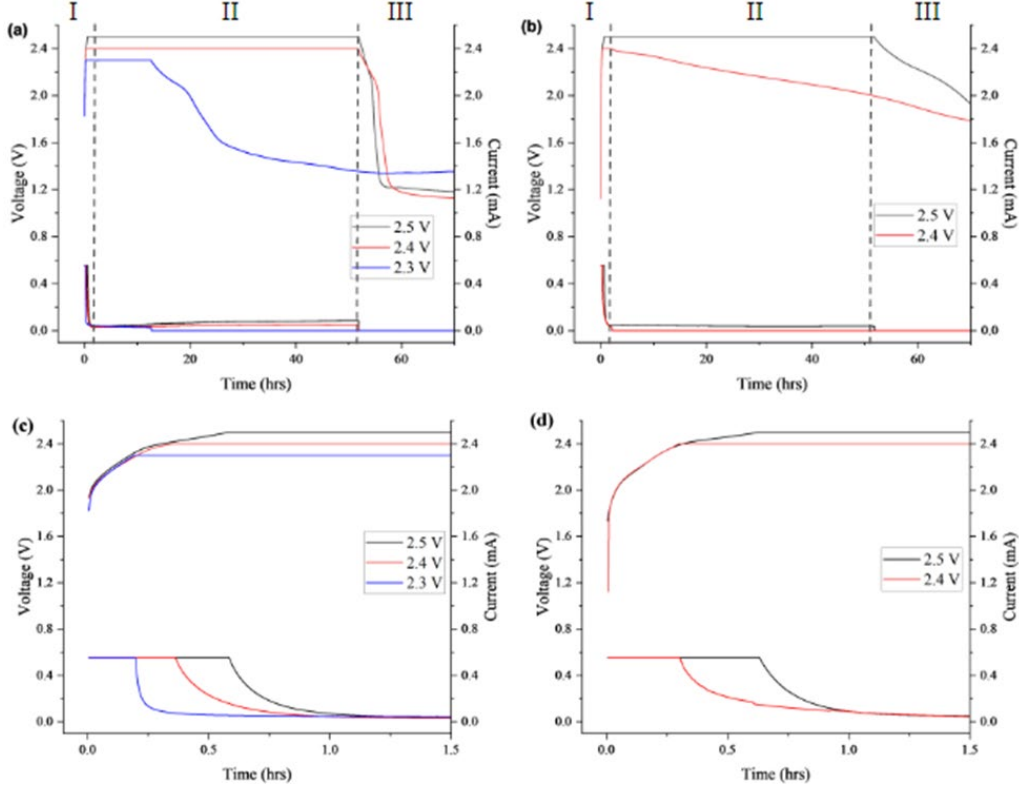


Fig. 4 Storage test with various UCVs: storage tests for WiSE coin cells with (a) uncoated TNO anodes, and (b) TNO anodes coated with 0.2% LATP (lithium aluminum titanium phosphate), with (c) and (d) showing the constant-current Phase I for each setup

From the tests conducted, the UCV has a clear effect on the degree of parasitic reactions in WiSE cells. This is logical and expected, as the lower upper-cutoff potential reduces the energy available to initiate certain reactions such as HER. However, note that even at the lowest cutoff voltage tested, 2.3 V, the cell is still not in equilibrium during the rest phase despite the extremely low capacity, which results from the reduced voltage. This implies that the lower UCV is not sufficient to enable the retention of Li-ions, or that the anode may require further optimization in the form of additional treatment (additives, surface coatings, etc.). Furthermore, it is possible to relate the amount of parasitic current at a particular UCV with the irreversibility or coulombic inefficiency within certain windows of operations. For instance, at a UCV of 2.6 V, at least 10% of the applied current likely goes to parasitic reactions by taking the quotient of the Stage II constant current and dividing it by the applied current.

A summary of the overall cell configuration and performance is given in Table 2. The decrease in electrochemical performance is summarized in the bottom four rows for future context. Note that the negative-to-positive (n/p) capacity ratio for these cells is greater than 1 to better understand the impact of the additives on anode performance with a large Li reservoir. Future experiments would likely need a more

balanced n/p ratio (= 1) to eliminate excessive electrode material, which significantly lowers the overall energy density and increases the cost. Using thinner separator layers, rather than the thick and porous quartz microfiber membrane (~475 μm thick), is an important future direction to reduce the electrolyte loading and improve energy density. Other factors such as electrode materials, current collectors, and loading can be further optimized but consist of commercially viable choices.

Table 2 Electrode specification and energy density calculations. Note that the baseline aqueous and organic electrolyte refers to the 20.0-m LiTFSI WiSE solution and 1-M LiPF₆ in EC:EMC (3:7), respectively.

Specification	Positive electrode	Negative electrode
Material	LMO	TNO
Composition	LiMnO ₂	TiNb ₂ O ₇
Electrode density (g cm ⁻³)	1.065	0.737
Coating thickness (μm)	125	45
Loading (mg cm ⁻²)	13.32	3.32
CC	Aluminum	Aluminum
CC thickness (μm)	27	27
Stack mass (mg cm ⁻²)	17.85	4.24
Theoretical cap. (mAh cm ⁻²)	1.678	1.106
Separator (mat. + μL)	Whatman QM-A Quartz Microfiber Separator (475 μm) + 100 μL	
Theoretical n/p ratio	1.52	
Specification	WiSE	Organic
Avg. discharge voltage (V)	2.004 (−12%)	2.29
Capacity (mAh) (2.6 UCV)	0.36 (−28%)	0.5
Stack volumetric energy	37.5 (−37%)	59.6
Density (Wh L ⁻¹)		
Stack specific energy	28.9 (−37%)	45.8
Density (Wh kg ⁻¹)		

4. Hybrid Electrolyte Studies

Another type of electrolyte, “HTE-21,” was considered for this study because another study using a similar electrolyte yielded promising results.¹² The HTE-21 electrolyte developed consisted of a 70% LiTFSI, 25% triethyl phosphate (TEP), and 5% H₂O solution (Fig. 5). Tests were conducted using similar coin cell builds and cycling procedures using Mg(TFSI)₂ and PEG as additives. The resulting coin cells had different properties when cycling compared with WiSE, as they were able to hold voltage in a storage test much better, but overall they had inferior capacity retention and energy density values. A possible reason for the cycling performance is poor wetting of the electrodes, as the HTE-21 electrolyte was much more viscous than the WiSE and thus would not be able to wet the surfaces as easily. Regardless, HTE-21 as an electrolyte will require further research and development to compare with the current state of the art in aqueous batteries.

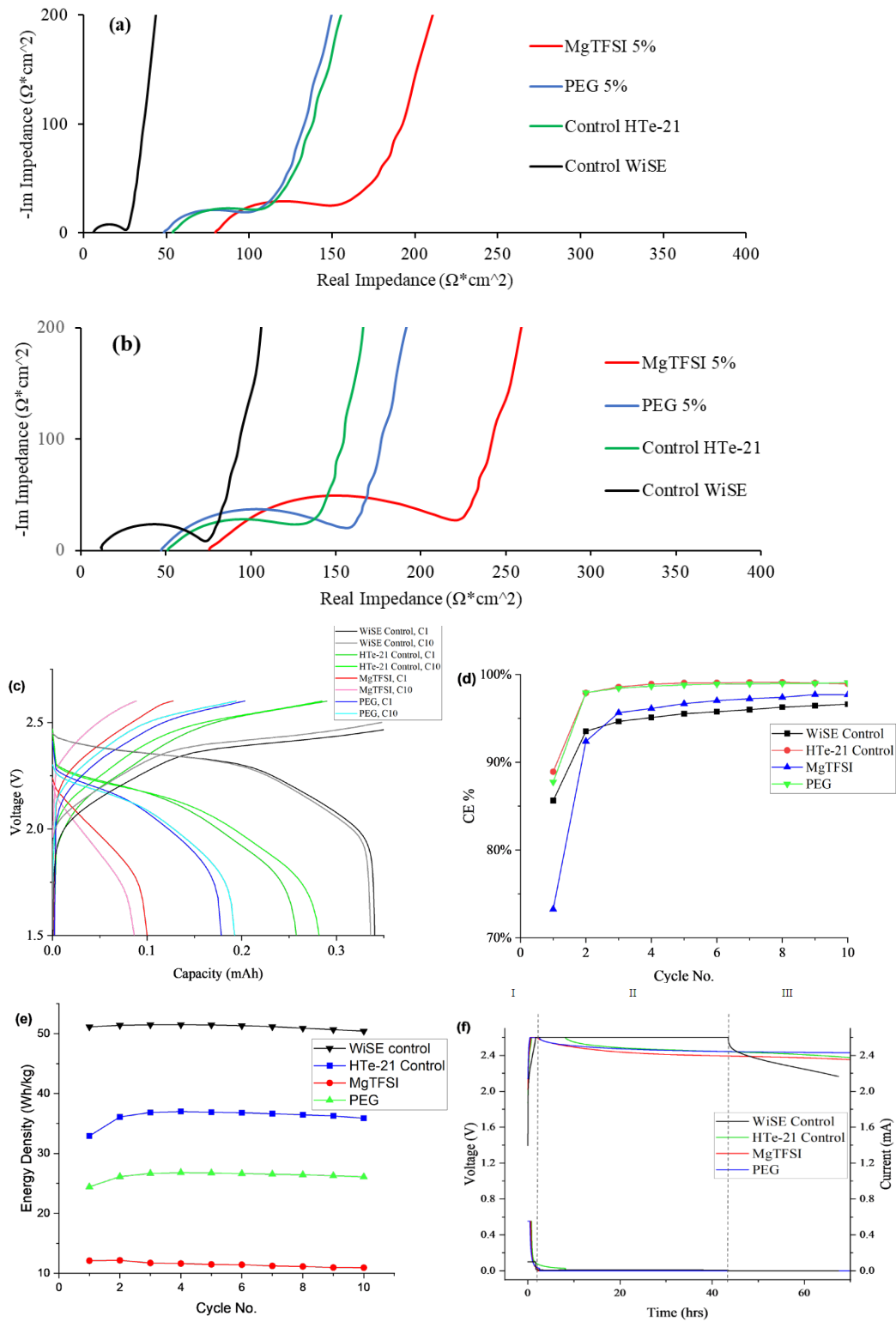


Fig. 5 HTe-21 cell data: EIS data (a) before and (b) after cycling; (c) voltage vs. capacity; (d) coulombic efficiency; (e) stack energy density; and (f) storage test data taken after cycling for hybrid cells, with MgTFSI and PEG additives at 5 wt% of the electrolyte mixture. Data from a WiSE control cell is added for comparison.

5. C4V Cathode Study

A series of tests was also performed with a nonconventional electrode, C4V, consisting of iron, manganese, and phosphate. The same list of 10 additive species was screened with this cathode in the baseline WiSE electrolyte. Impedance and cycle life were evaluated from various experiments, but none of the cells with the C4V cathode generated greater than 10 mAh g⁻¹ discharge capacity. Further investigation of the failure mechanism(s) is the focus of future studies.

6. X-ray Photoelectron Spectroscopy (XPS) Analysis of Selected Anodes

XPS was performed to look at the elemental content of the TNO electrodes after cycling (Fig. 6). In the C 1s spectra, a small peak between 290–294 eV is observed, which is attributed to the presence of C–F bonds in the SEI. This proves that the anodes did in fact have interphases form during testing. Another notable point was the similarities of the Mn and Fe peaks along all four anode samples. The C4V-based cell cycled poorly, and the expected reason behind this was that the C4V cathode had corroded during the testing phase. However, a corrosion process would have pushed Mn and Fe atoms into the anode, and no notable differences were observed between the peaks of the C4V data compared with those of the other samples. This implies that a different mechanism is responsible for the poor performance of the C4V-based cells, such as poor Li-ion release or insufficient wetting of the cathode surface.

The other elemental analyses display peaks that remain within the expected values. A phosphorus peak appears only in the HTe-21-based cell, which is logical considering that only that cell cycled with an electrolyte containing TEP. Similarly, the only anode that demonstrated a notable Mg peak was the one cycled with the MgTFSI–WiSE electrolyte mixture.

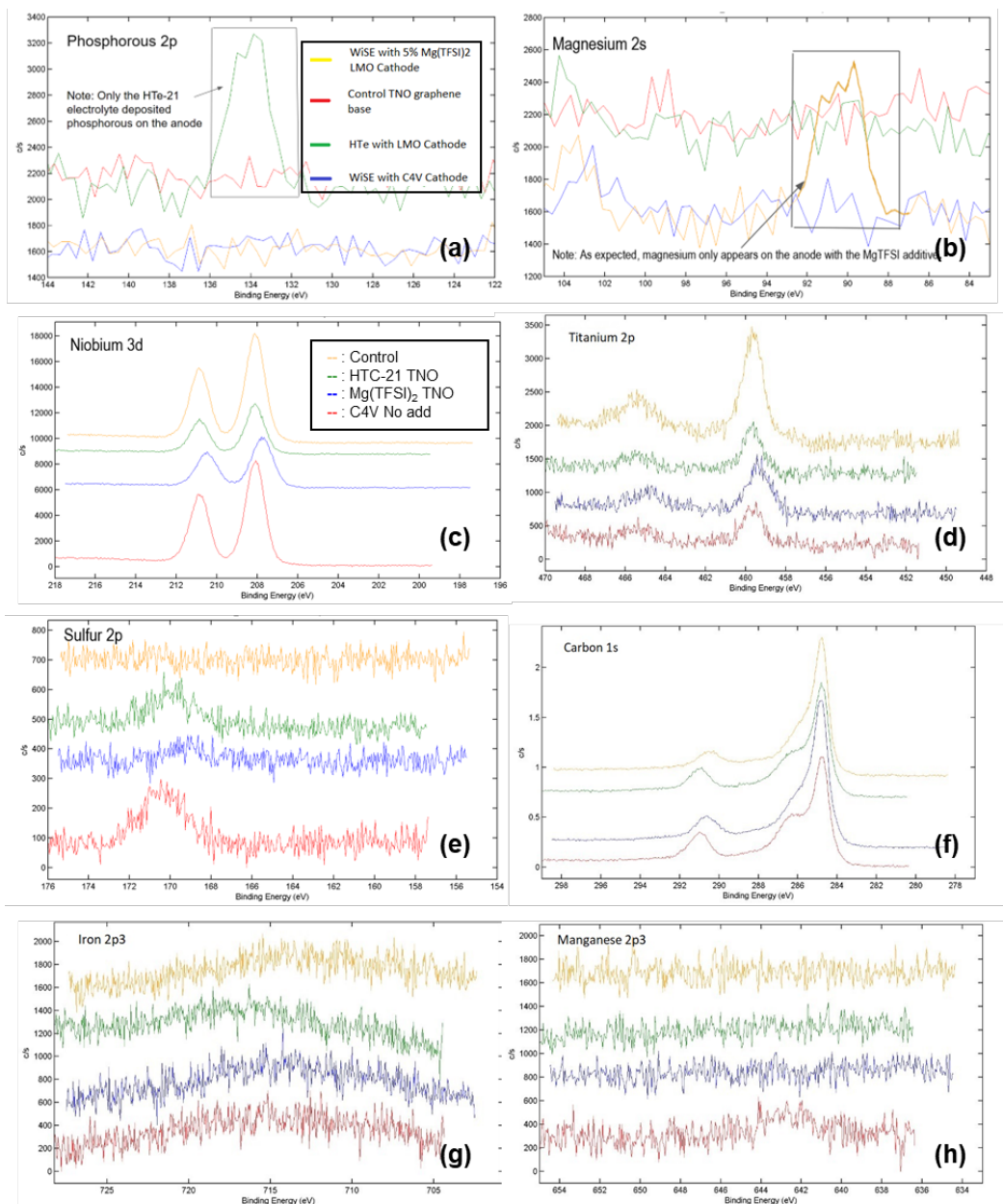


Fig. 6 XPS of the TNO anode before and after cycling in various electrolytes: XPS measurements for several critical elements on the TNO anodes used in the coin cells

7. Conclusions

Ten additives were tested in WiSE with an LMO–TNO full cell at 30 °C and down-selected based on performance relative to 1) solubility, 2) impedance, 3) short-term cycling stability, and 4) storage performance. None of the additive-based electrolytes outperformed the baseline WiSE system in the short-term cycling or storage performance. Most blends had a detrimental impact on capacity, coulombic efficiency, and lifetime. Additionally, the baseline WiSE electrolyte suffered a 37% drop in energy density relative to the baseline organic electrolyte. Storage tests also offer a sharp contrast in stability and performance between the baseline WiSE and organic electrolyte, with the former unable to avoid deleterious self-discharge (>100 mV) within 1 h or so of storage. This behavior appears independent of the UCV, although the degree of parasitic current during the constant voltage step of the storage test is highly correlated with the cell potential. Based on these sobering results, it is critical to identify improvements to the interphase stability such that cells can be stored in a charged state and significant capacity loss can be avoided in the activation cycles. More holistically, this study reveals the challenges associated with screening additives for aqueous electrolytes and suggests that additional steps are required to reduce the catalytic activity of the anode at high cell potentials. This study also provides information regarding the viability of certain additive mixtures and can be used to aid in screening for future additives based on similarity in structure and mechanisms.

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List of Symbols, Abbreviations, and Acronyms

AC	alternating current
C	carbon
CC	current collector
DC	direct current
DEC	diethyl carbonate
EC	ethylene carbonate
EIS	electrochemical impedance spectroscopy
F	fluorine
Fe	iron
H ₂ O	water
HER	hydrogen evolution reaction
LATP	lithium aluminum titanium phosphate
Li	lithium
LiPF ₆	lithium hexafluorophosphate
LiTFSI	lithium bis(trifluoromethanesulfonyl) imide
LMO	lithium manganese oxide
M	molarity
m	molality
Mg	magnesium
Mn	manganese
N/A	not applicable
Nb	niobium
n/p	negative to positive
O	oxygen
OCV	open-circuit voltage
PEG	poly(ethylene) glycol

PVDF	polyvinylidene fluoride
SEI	solid-electrolyte interphase
TEP	triethyl phosphate
TFSI	bis(trifluoromethanesulfonyl) imide
Ti	titanium
TNO	titanium niobate
UCV	upper cutoff potential
WiSE	“water-in-salt” electrolyte
XPS	X-ray photoelectron spectroscopy

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