UTS UNIVERSITY OF TECHNOLOGY SYDNEY

Investigation into Non-Flammable Electrolytes for Lithium and Zinc Secondary Batteries

by Pauline Jaumaux

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Prof. Guoxiu Wang, Asst. Prof. Dong Zhou and Dr. Bing Sun

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Pauline Jaumaux declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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List of publications

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3. **Pauline Jaumaux**[1], Junru Wu[1], Devaraj Shanmukaraj[1], Yizhou Wang, Dong Zhou, Bing Sun, Feiyu Kang, Baohua Li, Michel Armand, and Guoxiu Wang, Non-Flammable Liquid and Quasi-Solid Electrolytes toward Highly-Safe Alkali Metal-Based Batteries. ***Adv. Funct. Mater.***, 2021, 31, 2008644. DOI: 10.1002/adfm.202008644

4. **Pauline Jaumaux**[1], Qi Liu[1], Dong Zhou, Xiaofu Xu, Tianyi Wang, Yizhou Wang, Feiyu Kang, Baohua Li, and Guoxiu Wang, Deep-eutectic-solvent-based self-healing polymer electrolyte for safe and long-life lithium-metal batteries. ***Angew. Chem. Int. Ed.***, 2020 59, 9134-9142. DOI: 10.1002/anie.202001793. *Incorporated in this thesis as Chapter IV*.

5. Jiahui Lu[1], **Pauline Jaumaux**[1], Tianyi Wang, Chengyin Wang and Guoxiu Wang, Recent Progress in Quasi-Solid and Solid Polymer Electrolytes for Multivalent Metal Ion Batteries. ***J. Mater. Chem. A***, 2021, 9, 24175-24194. DOI: 10.1039/D1TA06606D

6. Qi Liu[1], Yizhou Wang[1], Xu Yang, Dong Zhou, Xianshu Wang, **Pauline Jaumaux**, Feiyu Kang, Baohua Li, Xiulei Ji and Guoxiu Wang, Rechargeable anion-shuttle batteries for low-cost energy storage. ***Chem***., 2021, 7, 1993-2021. DOI: 10.1016/j.chempr.2021.02.004

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9. Jian Yang, Weizhai Bao, **Pauline Jaumaux**, Songtao Zhang, Chengyin Wang and Guoxiu Wang, MXene-based composites: synthesis and applications in rechargeable batteries and supercapacitors. ***Adv. Mater. Interfaces***, 2019, 6, 1802004. DOI: 10.1002/admi.201802004

10. Tuhin Subhra Sahu[1], Sinho Choi, **Pauline Jaumaux**, Jinqiang Zhang, Chengyin Wang, Dong Zhou and Guoxiu Wang, Squalene-derived sulfur-rich copolymer@ 3D graphene-carbon nanotube network cathode for high-performance lithium-sulfur batteries. ***Polyhedron***, 2019, 162, 147-154. DOI: 10.1016/j.poly.2019.01.068

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Figure 5.7. Radial distribution functions g(r) of Li-O(H_2O), Li-O(NO_3^-), and Li-O(PD) pairs calculated from MD simulation trajectories in (**a**) 12.5 m $LiNO_3$ in H_2O and (**b**) 12.5 m $LiNO_3$ in PD: H_2O electrolytes. A Li-O(PD) peak is identified at 1.85 Å in the 12.5 m $LiNO_3$ in PD: H_2O electrolyte, demonstrating the PD molecules can partially participate in the Li^+ solvation sheath and link them together via hydrogen bonding.·····*p.129*

Figure 5.8. (**a**) *In-situ* polymerization mechanism of the TEGDA monomer in the presence of LWIS electrolyte. An optical image of an as-prepared LWIS gel electrolyte membrane is shown in the right panel. (**b**) FT-IR spectra of TEGDA monomer and the polymer matrix of LWIS gel electrolyte. (**c**) Raman spectra of pure water and 12.5 m $LiNO_3$ in H_2O, 12.5 m $LiNO_3$ in H_2O: PD and LWIS gel electrolytes. (**d**) Ionic conductivities of 12.5 m $LiNO_3$ in H_2O, 12.5 m $LiNO_3$ in H_2O: PD and LWIS gel electrolytes as a function of temperature. The discrete points represent the experimental data while the solid lines represent VTF fitting results. (**e**) Flammability tests of 1 M $LiPF_6$ in EC: DEC (left panels) and LWIS gel (right panels) electrolytes.·····*p.131*

Figure 5.9. Pictures of the LWIS gel (**a**) at rest state and (**b**) under the pressure of a 100 g weight.·····*p.132*

Figure 5.10. (**a**) Ionic conductivities of the 25 m $LiNO_3$ in H_2O electrolyte as a function of temperature. (**b**) Viscosities of the 12.5 m $LiNO_3$ in H_2O, 25 m $LiNO_3$ in H_2O and 12.5 m $LiNO_3$ in H_2O: PD electrolytes at 25 °C.·····*p.133*

Figure 5.11. Chronoamperometry profile under a polarization of 1 V in (**a**) 12.5 m $LiNO_3$ in H_2O, (**b**) 12.5 m LiNO3 in H2O: PD and (**c**) LWIS gel electrolytes.·····*p.134*

Figure 5.12. Weight losses of 1 M $LiPF_6$ in EC: DEC, 12.5 m $LiNO_3$ in H_2O and LWIS gel electrolytes along with aging time at 25 °C.·····*p.135*

Figure 5.13. EIS spectra of Mo_6S_8||LMO cells with 12.5 m $LiNO_3$ in H_2O: PD electrolyte (blue) and LWIS gel electrolyte (pink) tested in a half-charged state in the initial cycle. Frequency range: 10^{-2} to 10^5 Hz; disturbance amplitude: 5 mV. The dot lines represent the fitting values from the equivalent circuit. The equivalent circuit is shown in inset.·····*p.135*

Figure 5.14. (**a**) CV curves of the Mo_6S_8 and LMO electrodes at 0.1 mV s^{-1} obtained with the LWIS gel electrolyte. The electrochemical window of LWIS gel electrolyte is presented for comparison. (**b**) Schematic of the electrochemical stability windows of different electrolytes and the redox voltages of Mo_6S_8 anode and LMO cathode. (**c**) Charge-discharge curves of Mo_6S_8||LMO full cells with 12.5 m $LiNO_3$ in H_2O electrolyte (inset) and LWIS gel electrolyte in the 25th cycle at 1 C. (**d**) Cycling performance of Mo_6S_8|LWIS gel electrolyte|LMO full cell at 1 C.·····*p.137*

Figure 5.15. Cycling performances of Mo_6S_8||LMO full cell with (**a**) 12.5 m $LiNO_3$ in H_2O, (**b**) 25 m $LiNO_3$ in H_2O and (**c**) 12.5 m $LiNO_3$ in H_2O: PD electrolytes. Inset of **Figure 5.15**b: image of the separator after dismantling the cell after 50 cycles. Crystals can be observed on the separator.·····*p.138*

Figure 5.16. (**a**) Rate performance and (**b**) corresponding charge-discharge curves of Mo_6S_8|LWIS gel electrolyte|LMO full cell.·····*p.139*

Figure 5.17. (**a, b**) TEM images of Mo_6S_8 anodes after 20 cycles in (**a**) 12.5 m $LiNO_3$ in H_2O and (**b**) LWIS gel electrolytes. (**c**) Schematic illustration of the SEI composition in the LWIS gel electrolyte. (**d, e**) Li 1s and (**f, g**) O 1s XPS spectra of Mo_6S_8 anode after 20 cycles in (**d, f**) 12.5 m $LiNO_3$ in H_2O and (**e, g**) LWIS gel electrolytes.·····*p.141*

Figure 5.18. TEM images of Mo_6S_8 anode after 20 cycles in (**a**) 25 m $LiNO_3$ in H_2O and (**b**) 12.5 m $LiNO_3$ in H_2O: PD electrolytes.·····*p.141*

Figure 5.19. (**a**) C 1s and (**b**) N 1s XPS depth profiling spectra of a Mo_6S_8 anode after 20 cycles in LWIS gel electrolyte. C 1s spectrum: C-F: 291.8 eV; C=O: 290.5 eV; C-O 287 eV; C-N: 285.5 eV ; C-C: 284.5 eV,[14] N 1s spectrum: LiN_xO_y: 399 eV, Li_3N: 397 eV; R-NO_2: 394.5 eV.[34]·····*p.142*

Figure 5.20. (**a**) Li 1s and (**b**) O 1s XPS depth profiling spectra of a Mo_6S_8 anode after 20 cycles in 12.5 m $LiNO_3$ in H_2O: PD electrolyte.·····*p.142*

Figure 6.1. Schematic of the mechanism of Zn/Li hybrid battery during charge and discharge with 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF molecular crowding electrolyte.·····*p.147*

Figure 6.2. (**a**) Solubility limit of LiOTf in several solutions containing 1 m $Zn(OTf)_2$. Inset: Picture of 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in NMF (left) and 7.7-H_2O: NMF (right). (**b**) Price comparison between the "water-in-salt" electrolyte (*i.e.*, 23 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O) and the molecular crowding electrolyte (*i.e.*, 7.7-H_2O: NMF). Inset: Corresponding volumetric mass. (**c**) Flammability test of a glass fibre separator soaked with 7.7-H_2O: NMF electrolyte.·····*p.151*

Figure 6.3. Mass loss of several electrolytes at room temperature and atmospheric conditions (7.7-H_2O electrolyte: 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O).·····*p.151*

Figure 6.4. (**a**) Linear sweep voltammetry spectra of 9.7 m LiOTf in H_2O: NMF with various H_2O to NMF mass ratio (H_2O: NMF mass ratio = 10-0 to 1-9). To avoid Zn deposition, 1 m $Zn(OTf)_2$ was replaced by 2 m LiOTf. (**b**) Electrochemical stability window of 7.7-H_2O: NMF electrolyte and 7.7-H_2O electrolyte which evidenced the Zn potential deposition and water decomposition.·····*p.153*

Figure 6.5. (**a**) Raman spectra and (**b**-**c**) FTIR spectra of the 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF with various H_2O to NMF mass ratio (H_2O: NMF mass ratio of 10: 0 to 1: 9).·····*p.154*

Figure 6.6. (**a**) Snapshots of the simulated cell with 7.7-H_2O (left) and 7.7-H_2O: NMF (right) after 20 ns at 298 K obtained with MD simulations. (**b**) Schematic representation of the solvation sheath of Zn cation in the corresponding electrolyte. The radial distribution function g(r) of Zn-O(OTf), Zn-O(H_2O) and Zn-O(NMF) pairs calculated from MD simulation trajectories in (**c**) 7.7-H_2O and (**d**) 7.7-H_2O: NMF. (**e**) Number of hydrogen bonds formed in 7.7-H_2O and 7.7-H_2O: NMF systems at 20 ns.·····*p.155*

Figure 6.7. The radial distribution function g(r) of Li-O(OTf), Li-O(H_2O) and Li-O(NMF) pairs calculated from MD simulation trajectories in (**a**) 7.7-H_2O and (**b**) 7.7-H_2O: NMF.·····*p.156*

Figure 6.8. (**a**) Cycling performance of Zn||LMO full cells with 7.7-H_2O (blue line) and 7.7-H_2O: NMF (pink line) electrolytes at 1 C. Charge and discharge curves of (**b**) Zn| 7.7-H_2O| LMO batteries and (**c**) Zn| 7.7-H_2O: NMF|LMO batteries at various rate from 0.1 C to 5 C and, (**d**) corresponding rate performance of Zn||LMO full cells with 7.7-H_2O (blue line) and 7.7-H_2O: NMF (pink line) electrolytes. (**e**) The evolution of interfacial resistance of Zn||LMO batteries with 7.7-H_2O (blue) and 7.7-H_2O: NMF (pink) electrolytes at 15 and 100 cycles.·····*p.158*

Figure 6.9. Ionic conductivity of various electrolytes. The experimental data is represented by the dots while the lines represent the Arrhenius fitting values.·····*p.159*

Figure 6.10. EIS spectra of the Zn||LMO cells with (**a**) 7.7-H_2O: NMF and (**b**) 7.7-H_2O electrolytes after 0, 15 and 100 cycles. The equivalent circuit is represented in the inset of **Figure 6.11**a. The dash lines represent the fitting values.·····*p.159*

Figure 6.11. Electrochemical performance of the Zn||LMO cells with 23 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O. (**a**) Electrochemical stability window of the 23 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O and 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF. (**b**) Long cycling performance of Zn||LMO batteries with 23 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O and 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF electrolytes. (**c**) Charge-discharge profile of Zn||LMO batteries with 23 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O electrolyte at different rate (0.1 C to 5 C). (**d**) Corresponding rate performances of Zn||LMO batteries with 23 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O and 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF electrolytes.·····*p.160*

Figure 6.12. Electrochemical performance of the Zn||LMO cells with 1m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF. (**a**) Electrochemical stability window of the 1 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF and 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF. (**b**) Long cycling performance of Zn||LMO batteries with 1 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF and 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF electrolytes. (**c**) Charge-discharge profile of Zn||LMO batteries with 1 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF electrolyte at different rate (0.1 C to 5 C). (**d**) Corresponding rate performances of Zn||LMO batteries with 1 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF and 7.7 m LiOTf + 1 m $Zn(OTf)_2$ in H_2O: NMF electrolytes.·····*p.161*

Figure 6.13. Static stability of zinc metal anode in pure H_2O (grey), pure NMF (green), 7.7-H_2O (blue) and 7.7-H_2O: NMF (pink) and the corresponding FE-SEM images.·····*p.162*

Figure 6.14. XRD profiles of the Zn metal after 49 days submerged in static stability of zinc metal anode in (a) pure H_2O, (b) pure NMF, (c) 7.7-H_2O and (d) 7.7-H_2O: NMF.·····*p.163*

Figure 6.15. pH value of different electrolytes.·····*p.163*

Figure 6.16. Symmetric Zn||Zn cell cycled with 7.7-H_2O: NMF. Inset: Zoom-in of the voltage profile after 140 h.·····*p.164*

Figure 6.17. Voltage profile of Zn||Zn symmetric cells with the 7.7-H_2O: NMF electrolyte at different current density. ·····*p.164*

Figure 6.18. CV of the Zn||LMO cell with 7.7-H_2O: NMF.·····*p.165*

Figure 6.19. FE-SEM images of the Zn anode after 5 cycles (**a-b**) and 25 cycles (**c-d**) in (**a-c**) 7.7-H_2O, (**b-d**) 7.7-H_2O: NMF.·····*p.166*

Figure 6.20. The Zn 2p, F 1s, S 2p and C 1s XPS depth profiling spectra of the Zn anode retrieved from Zn||LMO batteries after 25 cycles with (**a**) 7.7-H_2O and (**b**) 7.7-H_2O: NMF electrolytes.·····*p.167*

Figure 6.21. (**a**) Cyclic voltammograms of LMO cathode with 7.7-H_2O (blue line) and 7.7-H_2O: NMF (pink line) at 1 mV s^{-1}. (**b**) *In-situ* XRD patterns of LMO cathode during the 5^{th} cycle in 7.7-H_2O (left) and 7.7-H_2O: NMF (right) at 0.2 C. (**c**) Mn amounts on the separators after cycling for 25 cycles in 7.7-H_2O (blue) and 7.7-H_2O: NMF (pink) obtained with ICP-MS analysis. (**d**) XPS depth profiling presenting the Mn $2p_{3/2}$ spectra of LMO cathodes after 25 cycles with 7.7-H_2O (left) and 7.7-H_2O: NMF (right) electrolytes.·····*p.169*

ABSTRACT

Greenhouse gas emission related to the burning of fossil fuels for energy production is the main driver responsible for the climate crisis our society is facing. To avert climate change, the transition toward renewable energy production is urgent. However, the intermittence of these energy sources restrict their implementation. Coupling sustainable energy sources with energy storage systems could solve this issue. Since its commercialisation, Lithium (Li) -ion batteries have been at the centre of the attention for high-energy storage systems. As the global energy demand keeps increasing, new battery requirements are expected such as higher energy density and improved safety, which cannot be met by the current commercial Li-ion batteries. The thermally instable liquid electrolyte (containing highly flammable and toxic solvents, and thermally instable Li salts) usually employed in Li-ion batteries causes serious safety concerns. Many fires and explosions incidents occurred in the past few decades due to over-heating Li-ion batteries. Herein, various non-flammable electrolytes such as deep-eutectic-solvents and aqueous electrolytes were engineered to answer safety, dendrite growth and cost issues in Li and zinc (Zn) –based batteries. A fluorinated self-healing deep eutectic solvent quasi-solid electrolyte allowed long cycling performance of a Li-metal battery (Li||lithium manganese oxide ($LiMn_2O_4$, LMO) by creating a robust protective layer on the Li anode meanwhile the gel matrix helped guiding the Li deposition, thereby reducing dendrite growth and maintaining high safety. Then, a localized highly concentrated aqueous quasi-solid electrolyte was designed for low-cost Li-ion aqueous batteries with high voltage LMO cathode. Finally, a molecular crowding strategy was employed to suppress dendrite growth and corrosion on Zn metal anode in hybrid Zn||LMO aqueous batteries. These electrolyte designs opened up fascinating ways to tailor electrolyte properties for high safety and low-cost next battery generation.