Supporting Information

Stabilizing the Solid-Electrolyte Interphase with Polyacrylamide for High-Voltage Aqueous Lithium-Ion Batteries

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1 Experimental Procedures

1.1 Electrolyte and electrode preparation

LiTFSI and PAM were purchased from Abcr GmbH and Sigma Aldrich, respectively, and stored in an Argon filled glovebox. Deuterated PAM-D3 was purchased from Polymer Source and used in SANS measurements to facilitate the scattering contrast. The WiSE refers to a 21 mol kg\(^{-1}\) LiTFSI aqueous solution, while the series of “WiSE-P\(_{x}\)” (x=2.5, 5, and 7.5) electrolytes were prepared by dissolving the PAM powder in the WiSE at PAM: water mole ratios of x: 100.

The positive electrode contained LiMn\(_2\)O\(_4\) active material (Hunan Shanshan Advanced Materials Co. Ltd), Super C65 conductive carbon (IMERYS Graphite & Carbon) and the polyvinylidene difluoride (PVdF, Kynar® 761A, Arkema Group) binder at a weight ratio of 80:10:10, and stainless steel was used as current collector. The mass loading of active material was ~4 mg cm\(^{-2}\). Amorphous LiTi\(_2\)(PO\(_4\))\(_3\) coated anatase TiO\(_2\) (L-TiO\(_2\)) was used as negative active material, which was prepared according to our previous report\([1]\). The negative electrode contained L-TiO\(_2\), Super C65 and PVdF at a weight ratio of 80:10:10. Al foil was used as current collector, and the mass loading of active material was ~2 mg cm\(^{-2}\). Glass fiber fleece (Whatman GF/A) was used as separator.

A free-standing activated carbon electrode served as counter electrode for CV measurements, which was composed of DLC Super 30 (activated carbon, Norit), Super C65, and polytetrafluoroethylene (PTFE, binder, Sigma Aldrich) at a weight ratio of 85:10:5. The average mass of activated carbon was ~35 mg cm\(^{-2}\).

1.2 Material characterizations

Fourier-transform infrared spectroscopy (FTIR) spectra were obtained using a Vertex 70 FT-IR spectrometer (Bruker) connected with an attenuated total reflectance (ATR) unit. The ionic conductivity of the electrolyte was measured with MCS 10 conductivity meter (Biologic) with an integrated frequency response analyzer and a temperature control unit to maintain the temperature at 30 °C. The viscosity and density of different electrolytes were obtained with a kinematic viscometer (Anton Paar SVM 3001) at 30 °C. Differential scanning calorimetry (DSC) measurements were conducted on a DSC Q2000 (TA Instruments). All samples were initially equilibrated at 25 °C for 30 min, then cooled to -120 °C and subsequently heated to 60 °C. The cooling/heating rate was 2 °C min\(^{-1}\). For post-mortem characterization, stainless steel working electrodes were disassembled from the cells after linear sweep voltammetry (LSV) measurements and washed three times with 1,2-dimethoxyethane (DME) to remove the residual salts and then dried under vacuum for 12 hours at room temperature. The morphology of these electrodes was observed by a field emission scanning electron microscope (FE-SEM, Zeiss Auriga) at 3 kV and TEM (JEOL, JSM-2010) at an accelerating voltage of 200 kV. The chemical composition of the electrode surface was measured by XPS measurements with an AXIS Ultra DLD (Kratos; a focused 20-500 μm diameter beam of monochromatic X-rays; 15 kV filament voltage source energy).

1.3 Electrochemical measurements

LSV and cyclic voltammetry (CV) were performed on a VSP electrochemical workstation (Biologic) with three-electrode cells\([2]\). Stainless steel mesh and activated carbon were used as counter electrodes for LSV and CV measurements, respectively. Ag|AgCl was used as
reference potential, and the potential was converted to the value vs. Li|Li$^+$ when plotting, assuming that the potential of Ag|AgCl electrode is 3.239 V vs. Li|Li$^+$. 0.1 mV s$^{-1}$ was applied as the scan rate for CV measurements, the cell with L-TiO$_2$ negative electrode was cycled between 1.90 and 2.55 V vs. Li|Li$^+$, while a potential range of 4.0-4.6 V vs. Li|Li$^+$ was used for the one with LMO positive electrode. For LSV measurement, the potential was swept from open-circuit potential (OCP) to 0.5 or 5.5 V vs. Li|Li$^+$ with a scan rate of 0.2 mV s$^{-1}$. Galvanostatic cycling measurements were carried out on MACCOR series 4000 battery testers (Maccor Inc.) in a voltage range of 0.8-2.5 V for the full cells at 1 C rate (1 C=150 mA g$^{-1}$, the capacity was calculated based on the mass of L-TiO$_2$). The operating temperature was 20 °C for all electrochemical measurements.

1.4 Operando small angle neutron scattering (SANS)

Operando SANS measurements were performed on the KWS-1 instrument operated by the Jülich Centre for Neutron Science (JCNS) at Heinz Meier-Leibnitz Zentrum (MLZ), Garching, Germany[3]. Symmetric pouch cells with stainless steel as both working and counter electrodes were used for SANS measurements. Ag|AgCl electrode and glass fiber fleece (Whatman GF/D) were used as reference electrode and separator, respectively. The geometric instrument settings of SANS were 8m/8m and 4m/2m collimation/detector distance. The neutron velocity selector with a wavelength spread of 10% (full width at half maximum) selected $\lambda = 5$ Å neutrons. The $^3$He detector had an area coverage of approx. 1 m$^2$. The intensities $dI/dQ$[cm$^{-1}$] have been calibrated by a secondary plexiglass standard after subtracting all background and taking pixel sensitivity into account. The scattering vector $Q = 4\pi/\lambda \sin (\theta/2)$ is calculated based on the geometric scattering angle $\theta$. Data reduction was performed using the QtiKWS software provided by JCNS.

The Porod law states that for sharp surfaces the scattering law $I(Q) = 2\pi(\Delta \rho)^2Q^{-4}$ is observed on length scales larger than the particular particle size. The scattering length density difference $\Delta \rho$ is also called contrast. The power law $Q^{-4}$ is characteristic for sharp (non-smooth) surfaces. The surface per volume $S/V$ is the physical underlying observed magnitude. Thus, the observed intensity at a fixed Q-vector directly scales with the characteristic surface in the material.

1.5 Density functional theory (DFT) calculations

Reduction potentials for salt and PAM contributions to the SEI were computed using Gaussian 16 rev. C01 at the SMD (acetone, dielectric constant $\varepsilon=20$)/M052X/6-31+G(d,p) level of theory using a methyl-capped trimer as an model compound for the PAM polymer[8]. Acetone is used as the solvent to reflect the decreased dielectric constant in WiSE. Trimer configurations were sampled using the conformer search tools in Materials Studio[5] with the COMPASS II force field[6], several low lying minima were further screened via full geometry relaxation at the above DFT level. The molecular editor Avogadro[7] was used to sample configurations of PAM with LiTFSI species present using the built-in MMFF94 force field[8]. After an initial optimization with DFT, some of the low free energy structures would be manipulated by hand in Avogadro to further clean them up (e.g., to ensure Li-F-Li forms as in Figure 4b). These structures would be optimized again. Collectively 50-60 unique configurations were sampled at the DFT level to determine the reduction potentials in Figures 4, S3, and S4. Only the highest reduction potentials are reported as these correspond to the most thermodynamically favorable species. The reduction potential is computed from free energy differences ($\Delta G_{298}$) in the optimized reduced and non-reduced species at 298.15 K,

$$E^{red} = -\frac{\Delta G_{298}^S}{nF} - 1.4 \text{ V}$$

where F is Faraday’s constant and n is the number of electrons added to reduce the species. The 1.4 V shift adjusts the result to the Li|Li$^+$ scale, an error on the order of ~0.1 V is expected from the choice of proton solvation free energy[9] in addition to errors due to the limited sampling of the (non-)reduced species.[10] Additionally, comparing previous results of the reduction potential of LiTFSI aggregates in WiSE[11] to Figure S3, it is clear the balance of explicit vs implicit solvation is one of the more significant sources of error in such calculations. Generally, relying on implicit solvation to ‘complete’ the solvation shell of a cation tends to increase the reduction potential computed relative to adding explicit solvent (or other coordinating species like PAM in this case).
Figure S1. Differential scanning calorimetry (DSC) curves of a series of WiSE-P_x electrolytes (x=0, 2.5, 5, 7.5) recorded during scans from 25 to -120 °C and back to 60 °C. All scan rates were set to 2 °C min⁻¹. The peritectic temperature and the liquidus transition temperature are named as $T_p$ and $T_L$, respectively.

Figure S2. Scatter plots of operando SANS experiments for cells (a) with WiSE and (b) with WiSE-P_5 when scanning to high potential.
Figure S3. Reduction potentials (in Volts) vs Li/Li+ of LiTFSI (simulating salt aggregation in WiSE) with the SMD(acetone)/M052X/6-31+G(d,p) model chemistry. The green arrow follows defluorination and blue follows S-N cleavage.

Figure S4. (a) Reduction potentials (in Volts) vs Li/Li+ of lithiated polyacrylamide to form LiOCN (left) and a urea analogue from an isocyanic acid intermediate (right) both computed at the SMD(acetone)/M052X/6-31+G(d,p) level of theory. Mobile protons are labelled with asterisks.
Figure S5. SEM images of stainless-steel working electrodes after LSV measurements scanning to 1.9 V in WiSE (a) and WiSE-P$_5$ (b).

Figure S6. Illustration of the evolution of SEI formation at (a) 1.9 V and (b) 0.5 V (vs. Li$|\text{Li}^+$) in WiSE, (c) 1.9 V and (d) 0.5 V (vs. Li$|\text{Li}^+$) in WiSE-P$_5$, respectively.
### Table S1. Physicochemical properties of WiSE-P\(_x\) electrolytes (\(x = 0, 2.5, 5\) and 7.5).

| Sample acronym | Density (g cm\(^{-3}\)) | Viscosity (mPa s) | Conductivity (mS cm\(^{-1}\)) |
|----------------|--------------------------|-------------------|-------------------------------|
| WISE           | 1.698                    | 47.4              | 8.3                           |
| WISE-P\(_{2.5}\) | 1.690                    | 610.2             | 7.8                           |
| WISE-P\(_{5}\)  | 1.675                    | 1679.8            | 6.5                           |
| WISE-P\(_{7.5}\) | -                       | -                 | 6.3                           |

All data was collected at 30 °C.
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4 Author Contributions

X.H. performed the experiments and wrote the original draft. R. W. performed Operando SANS measurements and wrote the corresponding part. T. P. performed the DFT simulations and wrote the corresponding part. X. J., L. D. and E. P. gave advice for the paper structure. X. H. and J. L. proposed the topic and supervised the work of X. H. and corrected the original draft. H. F., L. B., O. B., K. X., and M. W. corrected the original draft. All authors discussed the results and reviewed the final manuscript.