Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Towards high rate Li metal anodes: Enhanced performance at high current density in a superconcentrated ionic liquid

Kalani Periyapperuma,[a] Elisabetta Arca,[b] Steve Harvey,[b] Chunmei Ban,[b] Anthony Burrell,[b] Douglas R. MacFarlane,[c] Cristina Pozo-Gonzalo,[a] Maria Forsyth[a] and Patrick C. Howlett[a,*]

[a] ARC Centre of Excellence for Electromaterials Science, Institute for Frontier Materials, Deakin University, Melbourne, Victoria 3125, Australia

[b] National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA.

[c] ARC Centre of Excellence for Electromaterials Science, School of Chemistry, Monash University, Victoria 3800, Australia

[*] Corresponding author: *patrick.howlett@deakin.edu.au*

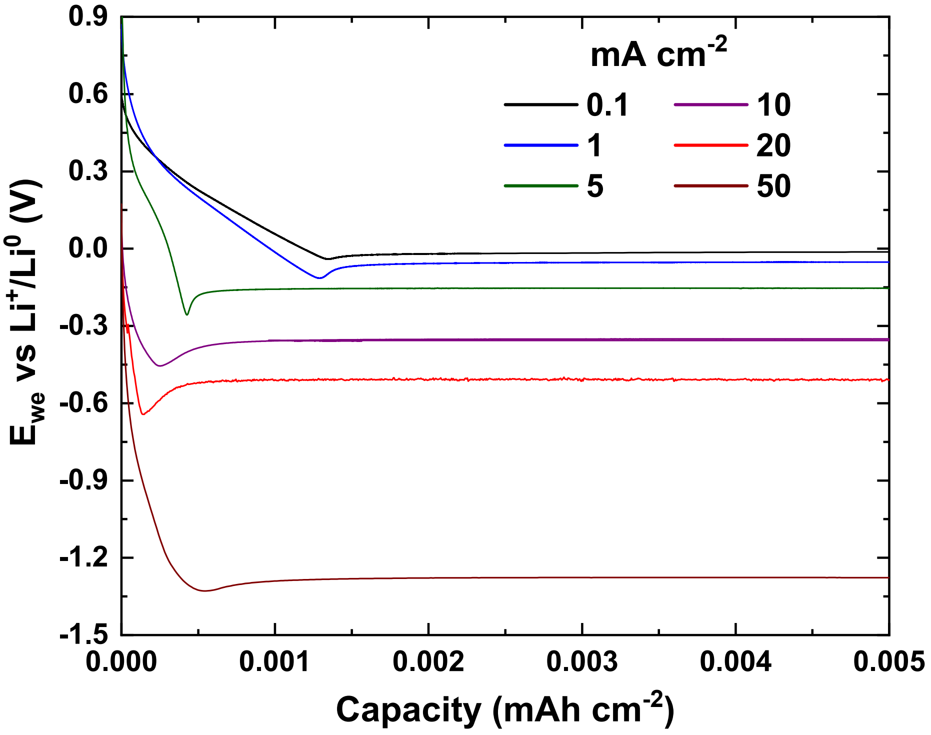

Figure S1 – Magnified view of the voltage profiles for Li nucleation from 0.1 to 50 mA cm^{-2} in 3.2 mol kg^{-1} LiFSI in [C_3mpyr][FSI] IL electrolyte at 50 °C.

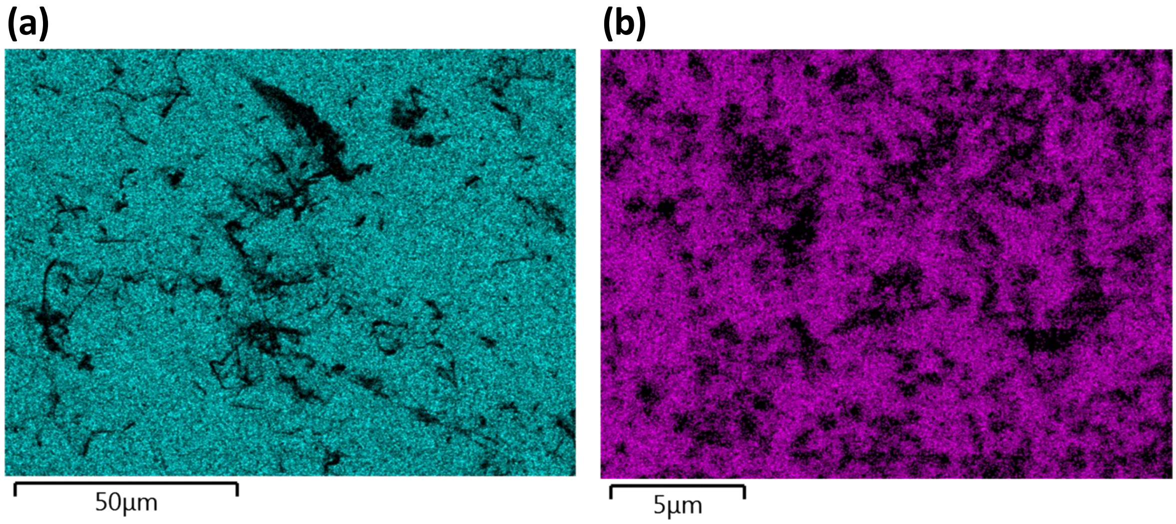

Figure S2 – The EDX mapping of Ni substrate surfaces after depositing Li at (a) 1 and (b) 20 mA cm^{-2} for 0.05 mAh cm^{-2} in 3.2 mol kg^{-1} LiFSI in [C$_3$mpyr][FSI] IL electrolyte at 50 °C.

Experimental Methods

Materials:

N-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide ([C$_3$mpyr][FSI], purchased from the Australian Institute for Innovative Materials, University of Wollongong, purity: [Br$^-$], [K$^+$] <100 ppm) IL and lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%, CoorsTek USA) salt were dried separately under high vacuum at 55 °C for 72 hours prior to use. The water content of the dried IL was <50 ppm. The electrolyte was prepared by mixing dried LiFSI with [C$_3$mpyr][FSI] IL to achieve 3.2 mol kg^{-1} (50 mol%) concentration. It was stirred at 50 °C overnight in an Ar-filled glovebox to achieve complete salt dissolution prior to use. The 50 mol% LiFSI in [C$_3$mpyr][FSI] IL electrolyte, which is more concentrated than the traditional Li-ion battery electrolytes, is referred to as 'superconcentrated electrolyte' in the discussion. The superconcentrated electrolyte is liquid at room temperature.

Electrochemical characterisation:

Voltammetric experiments were performed on a Biologic SP-200 potentiostat using a three-electrode setup consisting of a 1.5 mm diameter Ni working electrode (WE, ALS Co. Ltd, Japan), 1 cm^2 surface area Li metal counter electrode (CE, 250 µm thick, purity > 99.9%, Sigma

Aldrich, USA) and a Li pseudo-reference electrode (RE). The Ni electrode was polished with alumina powder (0.3 µm, Buehler, USA) mixed with a few drops of deionised water on a clean polishing cloth (Buehler). The polished electrode was rinsed with deionised water, sonicated for 2 minutes, and dried at 40 °C under vacuum overnight prior to transferring it to an Ar-filled glovebox. An electrolyte volume of 1 ml was used in this cell configuration, and therefore referred to as a 'flooded cell' in this work. The chronopotentiometric measurements were collected at a current density ranging from 0.1 to 50 mA cm^{-2} after iR-compensation. All the experiments in this study were performed at 50 °C. The average cycling efficiencies were calculated using equation 1,[1] where N is the number of cycles, Qex is excess plated charge (1 mAh cm^{-2}) or '1 mAh cm^{-2} electrodeposit' during the first cycle and Qps is the cycled charge that is stripped or plated from or onto the 1 mAh cm^{-2} deposit at each subsequent cycle (0.25 mAh cm^{-2}). The number of cycles was counted as the voltage reached ~1 V (vs. Li), indicating the complete consumption of the active 1 mAh cm^{-2} electrodeposit.

$$Avg.\,Cycling\ Efficiency = 100 * \frac{NQps}{NQps + Qex}$$

The cycling efficiencies and Li surfaces reported in this work were reproduced in multiple experiments (three or more), and the replicate results were used for the evaluation of corresponding error percentages.

Surface characterisation:

Scanning Electron Microscopy (SEM) – The Li samples were prepared by depositing Li onto a masked Ni foil (99.99%, Alfa Aesar) with 2 mm diameter exposed area for 0.01, 0.025, 0.05 and 1 mAh cm^{-2} at 1 and 20 mA cm^{-2} at 50 °C. The Li electrodeposits were gently rinsed in dimethyl carbonate (DMC, Sigma Aldrich, ≥ 99%) to remove residual IL. The electrodes were dried under vacuum to completely evaporate the solvent prior to sealing in an air-sensitive SEM sample holder under Ar atmosphere. All the SEM measurements were taken on a JSM-IT300 SEM at an acceleration voltage of 5 kV and 30 pA probe current. The SEM images were also used for the nuclei size and nuclei density analysis in Figure 2. Energy Dispersive X-ray Spectroscopy (EDX, Oxford X-Max 50 mm^2 EDX detector, 5 kV accelerating voltage) was used to analyse the Ni surface after depositing Li at 1 and 20 mA cm^{-2} for 0.05 mAh cm^{-2}.

X-ray Photoelectron Spectroscopy (XPS) – The Li samples were prepared as previously mentioned. The Li deposits were washed with 3 drops of DMC, 3 times, and dried under vacuum for 20 minutes prior to mounting on an XPS sample study. All the XPS experiments were performed at the National Renewable Energy Laboratory (NREL - CO, USA) using a Physical Electronics 5600 photoelectron spectrometer with an Al K-α X-ray source (1486.7 eV) operated at a power of 350 W. High-resolution region spectra were acquired at 21.75 eV pass energy and 0.1 eV energy step. The spectrometer binding energy (BE) scale was calibrated by measuring the valence-band and core-level spectra from sputter-cleaned Au and Cu foils (E_F = 0.00 eV, Au $4f_{7/2}$ = 83.96 eV and Cu $2p_{3/2}$ = 932.62 eV). The pressure in the analysis chamber was lower than 7×10^{-10} torr. The XPS data processing and curve fitting was performed using Igor Pro with a custom program adapted from Schmid *et al.*[2] Relative sensitivity factors were taken from the 'Handbook of X-ray Photoelectron Spectroscopy'.[3] Peak areas were measured after Shirley background fitting and a Gaussian/Lorentzian algorithm (70:30%) was used to fit the peaks to obtain quantitative results. The fit produced an estimated ±10% error in the atomic concentration determined for each peak.

Time of Flight - Secondary Ion Mass Spectroscopy (ToF-SIMS) – The Li samples were prepared similar to XPS samples. All the ToF-SIMS experiments were performed at NREL using a ToF-SIMS V system (ION-TOF GmbH) with a dual beam and a 3-lens 30 kV BiMn primary ion gun. The depth profiling was accomplished using 1 kV oxygen and cesium-ion sputter beams with 3–5 nA sputter current. An electron flood gun was used to compensate for sample charging during the sputter process. A 200×200 μm^2 sputter area corresponding to 0.025 nm s^{-1} sputter rate was used in this work. The sputter rates were determined from a calibration with silicon oxide wafer using similar conditions to that of the Li sample measurements. This produced an estimated ±10% error for sputter rates.

References:

1. A. F. Hollenkamp, P. C. Howlett, D. R. MacFarlane, S. A. Forsyth, and M. Forsyth, US Pat., 7479353 B2 (2009).

2. M. Schmid, H. P. Steinrück, and J. M. Gottfried, *Surface and Interface Analysis*, 2014, **46**, 505–511.

3. J. F. Moulder, *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification & Interpretation of XPS Data*, Perkin-Elmer Corporation, United States, (1992).