Electrochemical deposition and pseudocapacitive behavior in urea–based quasi-ionic liquid electrolytes studied with X-ray absorption spectra

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Synthesis and characterization of materials

Urea−$LiPF_6$ (molar ratio 3.6) and urea−LiTFSI (molar ratio 3.2) quasi-ILs were prepared from $LiPF_6$ (99+%, Acros), LiTFSI (98+%, Acros) and urea (98+%, Acros), which were dried in vacuum at 110 ºC, 110 ºC and 60 ºC for 12 h, respectively.[1–5] The BMP-TFSI IL was prepared and purified by the procedures in the literature;[6] however, chlorobutane instead of iodobutane was employed in this study. For these ILs, the water content in the electrolyte was determined (Karl–Fischer titrator) to be less than 80 ppm. All electrochemical experiments were performed in an argon-purified glove box (MBraun, UNI LAB-B). Anhydrous metal chlorides, including $SnCl_2$ (99+%, Aldrich), $RuCl_3$ (99+%, Acros), $NiCl_2$ (99.9%, Aldrich), $CoCl_2$ (99.7%, Alfa Aesar), $MnCl_2$ (99.99%, Aldrich), and VCl_3 (99+%, Alfa Aesar) were used as received.

All electrochemical experiments were performed in a three-electrode cell regulated with a potentiostat (Autolab). A Pt wire (Alfa Aesar, 99.95%) immersed in ferrocene/ferrocenium (Fc/Fc^+ = 50/50 mol %) BMP-TFSI (N-butyl-N-methyl pyrrolidinium TFSI) solution contained in a glass tube with a porous Vycor tip (Bioanalytical Systems, MF-2042) served as a reference electrode.[6, 7]

The density, viscosity and conductivity of quasi-ILs were measured at 301 K according to procedures described.[6, 7] The surface morphology of the samples was probed with a scanning electron microscope (SEM, JEOL 7000F). With an ultramicrotome we prepared a Mn oxide section (thickness 40-60nm) for analysis with the transmission electron microscope (TEM, JEOL 2000F). The X-ray absorption measurements were conducted at BL07A and BL17C beamlines of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. A sealed spectro-electrochemical cell with a window (Kapton tape) transparent to fluorescence served for X-ray absorption measurements.

Natural graphite powder (particle size ~70 μm, purity 99.99%; Alfa Aesar) was oxidized according to a modified Staudenmaier method to produce graphite oxide (GO).[8] Graphite (5 g) was continuously stirred in a mixed solution of sulfuric acid (88 mL), nitric acid (45 mL) and potassium chlorate (55 g) for approximately 100 h. The resulting GO was rinsed with HCl aqueous solution (5 %) and washed repeatedly with deionized water until the pH of the filtrate was neutral. The product was dried and pulverized. The GO was rapidly heated (~30 °C/min) to 1050 °C in an inert atmosphere (Ar) and cooled in the furnace. After thermal exfoliation and reduction, graphene was produced.

Electrodes of MnO_2/graphene nanocomposite (MGN) were synthesized with ethanol-assisted graphene-sacrifice reduction.[9, 10] $KMnO_4$ served as the precursor, which was reduced with graphene and ethanol to form MnO_2. In one pot, $KMnO_4$ (0.1 M) was dissolved in KOH aqueous solution (0.2 M, 20 mL). In another pot, graphene was dispersed (with ultrasonication) in a mixture of ethanol and water (20 mL/10 mL). After combination of the two pots, vigorous stirring for 3 h ensured the complete reduction. The resulting precipitates were separated in a centrifuge followed by thorough washing with deionized water. All samples were dried overnight at 80 °C before analyses. Using the proposed ethanol-assisted graphene-sacrifice concept, we synthesized composites of MnO_2 and graphene (mass ratio 9/1, evaluated with TGA).

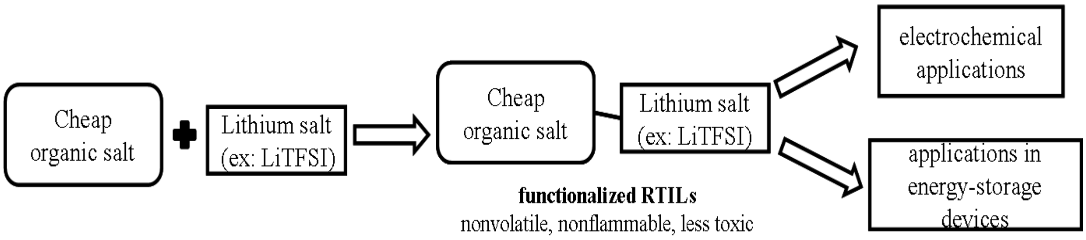

Fig. SI1†. Schematic illustration of the functionalized ILs attached to energy-storage devices and electrochemical applications.

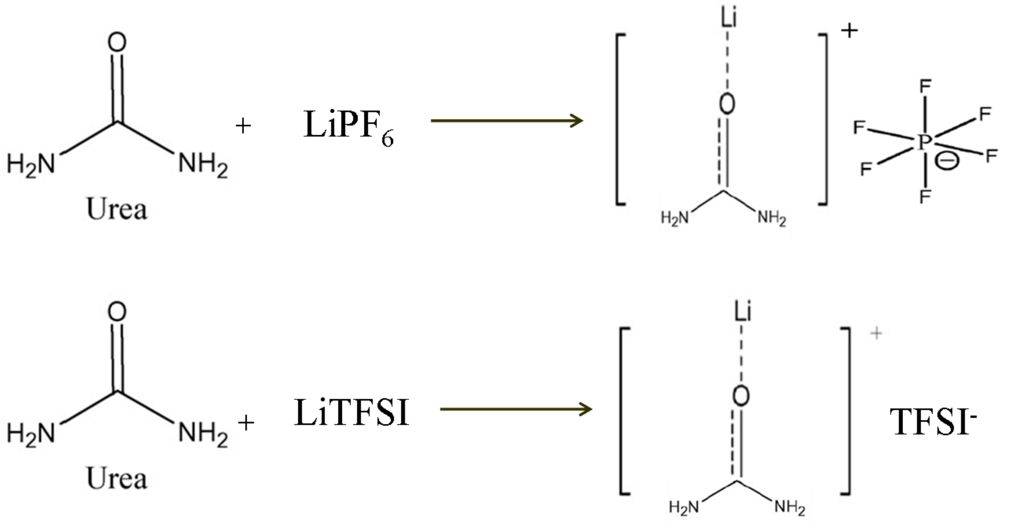

Fig. SI2†. The structure of urea–$LiPF_6$ and urea–LiTFSI, respectively.[5]

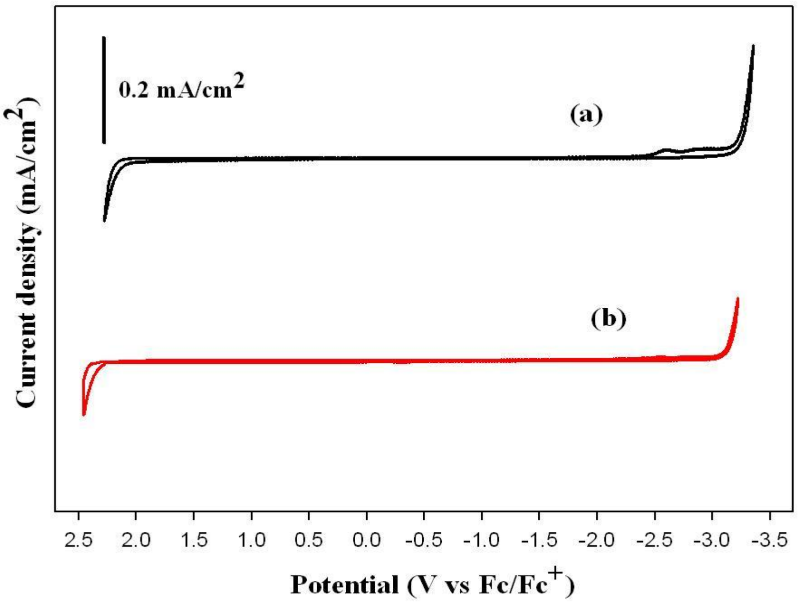

Fig. SI3†. The enlarged cyclic voltammograms of (a) blank urea−LiPF$_6$, (b) blank urea−LiTFSI at a Pt electrode.

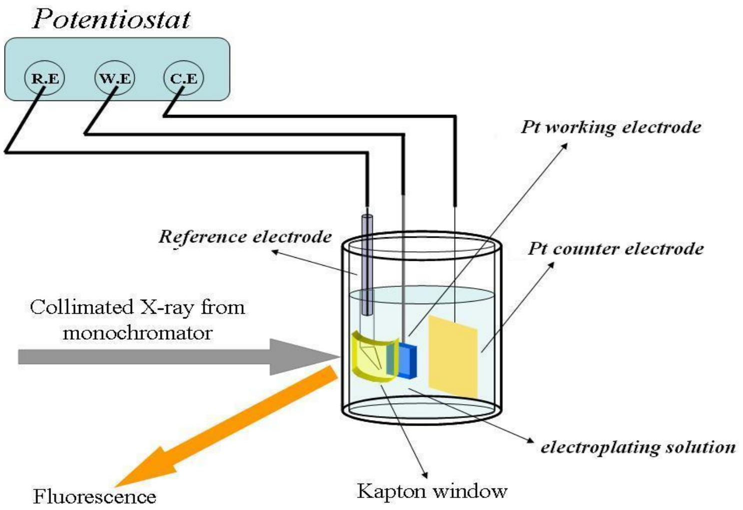

Fig. SI4†. Schematic illustration of the electrochemical cell used in the XAS studies. Before electrodeposition, the electroplating solutions were directly characterized with K-edge XANES spectra (without any electrode). After electrodeposition, the electrodeposited metal on substrates (without the cell) was characterized with K-edge XANES spectra.

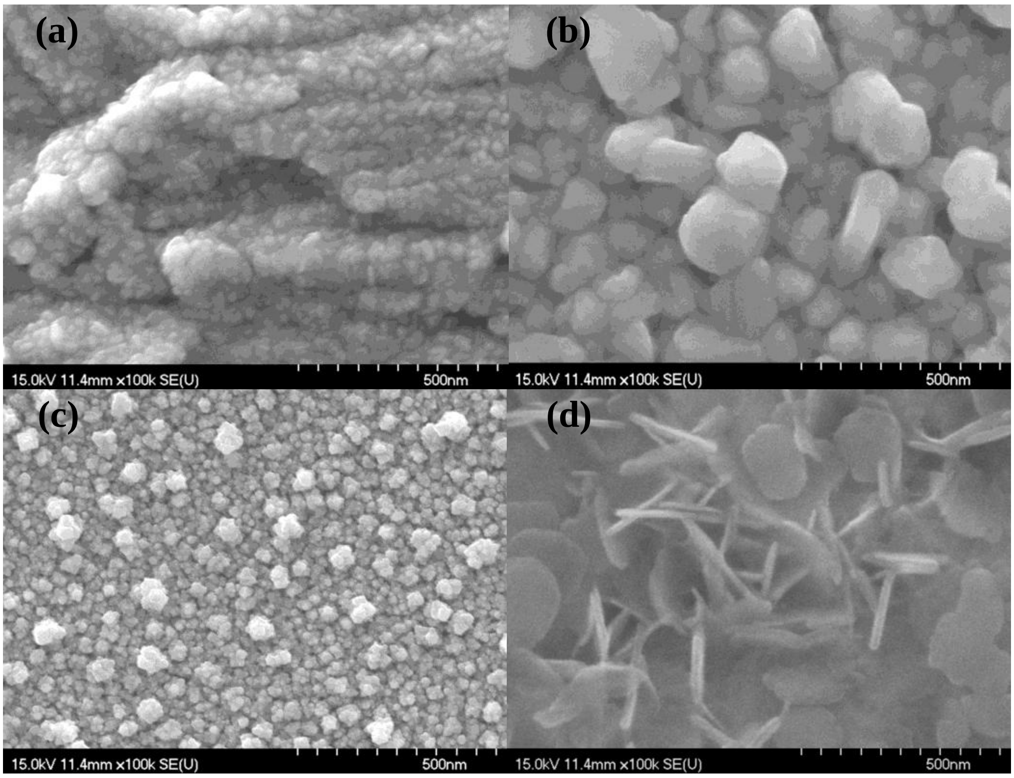

Fig. SI5†. SEM micrographs of the surface as deposited (a) Co,(b) Sn,(c) Ni, and (d) V, obtained from the urea-TFSI and urea−$LiPF_6$ quasi-IL, respectively.

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