

High-performance electrochemical pseudo-capacitor based on MnO₂ nanowires/Ni foam as electrode with a novel Li-ion quasi-ionic liquid as electrolyte

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Materials Synthesis and characterization

The LiClO₄-OZO quasi-IL with molar ratio 1:4.2 was prepared from LiClO₄ (Acros Inc., AP) and OZO (Acros Inc., 99 %), which were dried at 110 °C and at 55 °C for 12 h in vacuum, respectively.¹⁸ The melting point and boiling point of OZO is 89 °C and 220 °C, respectively. The content of water in the electrolyte was determined to be less than 80 ppm with a Karl-Fischer titration. Mn oxide was deposited anodically from Mn(CH₃COO)₂ aqueous plating solution (0.25 M) at room temperature, using a three-electrode electrochemical system. Ni foam (area ~1 cm²) was pretreated by degreasing in acetone, etching in hydrochloric acid, rinsing with water, soaking in 0.01 M MnCl₂ for 4 h, and rinsing again thoroughly with water, which, after drying, then served as the working electrode. A platinum sheet and a saturated calomel electrode (SCE) were assembled as the counter and reference electrodes, respectively. The electrodeposition was performed under a constant potential 0.45 V vs. SCE to give a total passed charge density 0.4 Coulombs/cm². The typical mass density, measured with a microbalance of accuracy 0.01 mg, of the deposited MnO₂ (thickness about 500 nm) was approximately 0.3 mg cm⁻². The

surface morphology of the MnO₂ electrode was probed with a scanning electron microscope (SEM, JEOL 6500F). With an ultramicrotome we prepared a Mn oxide section (thickness 40-60nm) for analysis with the transmission electron microscope (TEM, JEOL 2000F). A camera length 120 cm was adopted for the electron diffraction experiment. The electrochemical properties of the Mn oxide electrode in LiClO₄-OZO quasi-IL were characterized with cyclic voltammetry and chronopotentiometry at 25 °C in an argon-purified glove box (MBraun, UNI LAB-B) in which both moisture and oxygen content were maintained below 1 ppm. A Pt wire as a reference electrode was placed in a fritted glass tube containing N-butyl-N-methyl-pyrrolidinium-bis(trifluoromethylsulfonyl)imide (BMP-TFSI) IL with a ferrocene/ferrocenium couple as a potential standard (Fc/Fc⁺ = 50/50 mol %, potential +0.55 V vs. SHE). A spiral Pt wire as a counter electrode was directly immersed in the bulk LiClO₄-OZO quasi-IL. The applied potential and current were regulated with a potentiostat (AUTOLAB).

The variation of the oxidation state of Mn in the Mn oxide/Ni foam electrode was investigated at various applied potentials in LiClO₄-OZO quasi-IL with in-situ XAS spectrum recorded by the fluorescence-yield mode. A sealed spectro-electrochemical cell with a fluorescence-transparent Kapton tape window was used. Before measuring the absorption spectra at a given potential, we kept the electrode at a set potential for 15 min to allow the Mn oxide/Ni foam to attain a steady state. The in-situ XAS experiments were conducted at 07A1 beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The storage ring was operated with an electron energy of 1.5 GeV with a current of 360 mA. A double-crystal Si(111) monochromator served to tune the x-ray photon energy with energy resolution better than 0.3 eV. The X-ray absorption energy was calibrated using the known Mn K-edge absorption inflection point at 6539.0 eV of a Mn foil,

which was measured before each XAS scan.

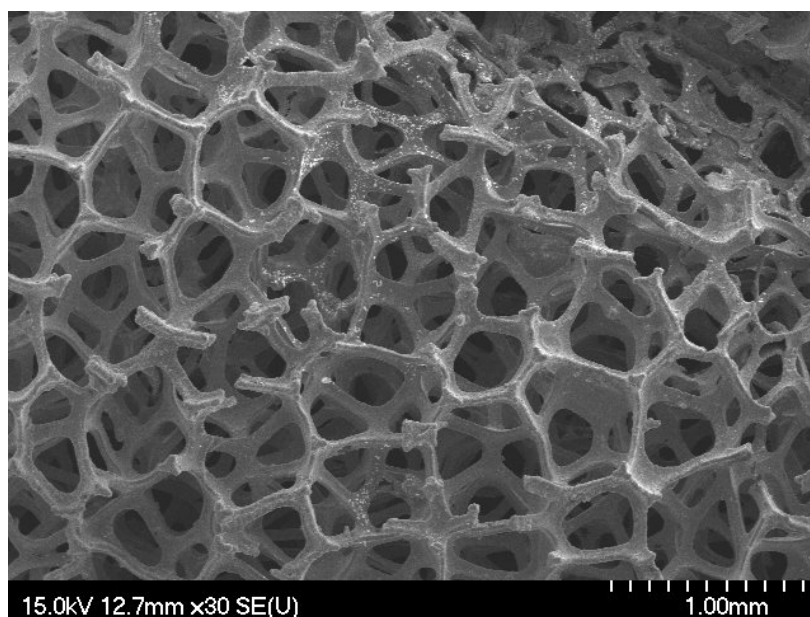


Fig. S1. SEM image of nickel foam

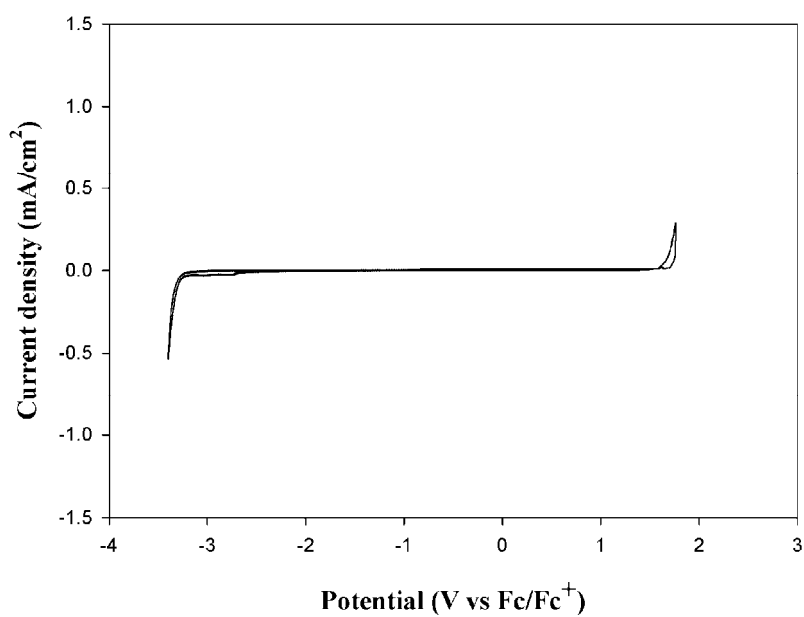


Fig. S2 CV of a glassy carbon electrode recorded in LiClO₄-OZO quasi-IL at potential sweep rate 5 mV/s.

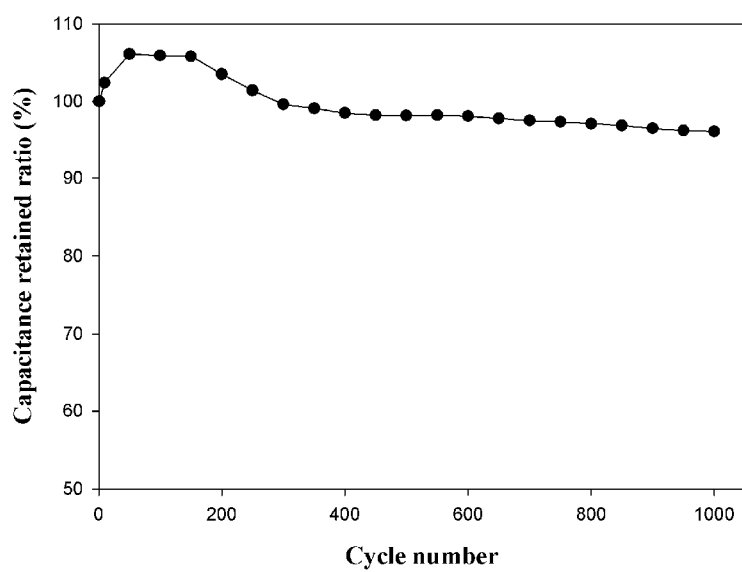


Fig. S3 Variation of oxide capacitance vs. CV cycle number measured in
 $\text{LiClO}_4\text{-OZO}$ quasi-IL.

Reference

R. J. Chen, F. Wu, L. Li, B. Xu, X. P. Qiu, and S. Chen, *J. Phys. Chem. C*, 2007, **111**,

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