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Supplementary Information

Building an Electrochemical Series of Metals in Pyrrolidinium-Based Ionic Liquids

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Experimental Methods

All metal foils (Ag, Cu, Sn, In, Zn, and Au) and Pt wire (0.25 mm dia.) were purchased form Alfa Aesar, Korea (purity 99.99%; other elements less than 1 ppm). [BMPyr] [NTf_2] and [BMPyr] [Nf_2] were purchased form C-TRI, Korea. [BMPyr] [NTf_2] and [BMPyr] [Nf_2] were dried in a vacuum oven at 100°C for 24 h to reduce residual water content. The ionic liquids were instantly transferred and stored in a nitrogen-filled glove box (Korea Kiyon, oxygen and moisture level less than 5 ppm) after vacuum drying the ionic liquids. All metal foil used as the working electrode was polished with alumina 0.05 μm on an alumina polishing pad (NeoScience, Korea). The counter and reference electrodes were polished with a SiC sand paper 1500 grid (DEERFOS, Korea). All polished electrodes were washed with an acetone (Sigma-Aldrich, 99.5%), rinsed with distilled water to remove residual alumina particles, and then dried 3 h at 100°C in an oven (Lenton Thermal Designs Ltd., UK) before usage.

All the electrochemical experiments were carried out at room temperature (298 K) using a three-electrode cell with a WPG100 potentiostat (WonATech) in a nitrogen-filled glove box. A three-electrode system, which consisted of a metal foil with different thicknesses as a working electrode (with a geometric area of 0.5 cm × 0.5 cm), Pt wire (0.5 mm in diameter) as a quasi-reference electrode, and coiled Pt wire (0.25 mm in diameter) as a counter electrode was employed. Ferrocene (Sigma-Aldrich, 98%) was prepared as an internal reference, and all potentials reported here were calibrated and converted based on a ferrocene/ferrocenium redox couple (vs. Fc/Fc^+). Electrochemical stability of neat ionic liquids was observed using an Au working electrode through cyclic voltammetry at a scan rate of 10 mV s^{-1}. Anodic linear sweep voltammetry (LSV) experiments were performed at a scan rate of 10 mV s^{-1}. After the anodic dissolution of metals, potentiodynamic polarization of the electrodes were carried out toward the cathodic direction with a potential scan rate of 2 mV s^{-1}.

Calculation of the amount of dissolved metals and their corresponding dissolution upper potential for 0.1 mM concentration

The amount of dissolved metal ions in 2 mL of 0.1 mM ionic liquid solutions is obtained as follows:

$$w_i = c_i \times M_i \times V \qquad (1)$$

where w_i is the amount of dissolved metal ions (g), c_i is the concentration of solution (0.1 mM), M_i is the molar mass of metal (g mol^{-1}), and V is the volume of solution (2 mL).

The dissolution potential for introducing the required amount (w_i) of metal ions can be calculated by Faraday's law as follows:

$$w_i = \frac{M_i \times Q}{n \times F} = \frac{M_i \times \int_{OCP}^{E_d} \frac{idE}{v}}{n \times F} \qquad (2)$$

where Q is the amount of electric charge for introducing the w_i of metal ions, n is the number of the mole of transferred electrons assuming normal oxidation states (1 for Ag and Cu, 2 for Sn and Zn, and 3 for In), F is the Faraday constant (96485 C mol^{-1}), E_d is the upper limit of the dissolution potential, OCP is the open circuit potential, i is the measured current in LSV, E is the potential, and v is the scan rate of LSV (10 mV s^{-1}).

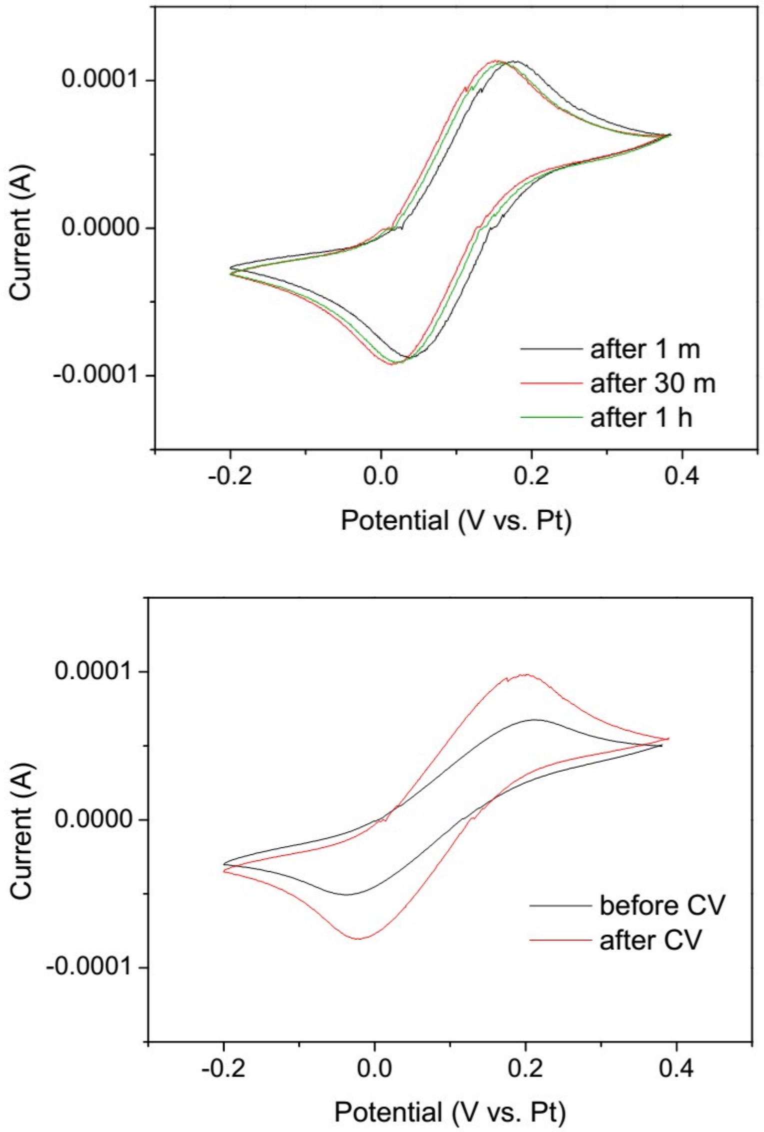
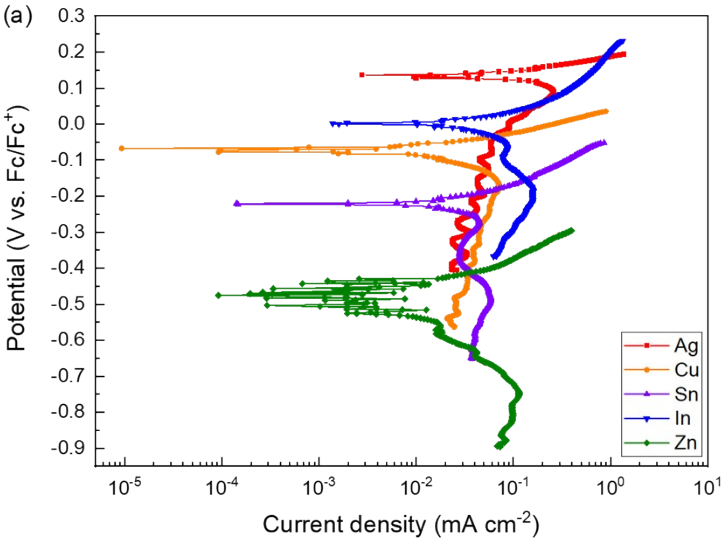


Figure S1. Cyclic voltammetry of Pt electrode with Fc/Fc$^+$ couple in [BMPyr] [NTf$_2$]: The potential fluctuation of Pt was less than 20 mV during 1 h storage in the electrolytes and before/after cyclic voltammetry.



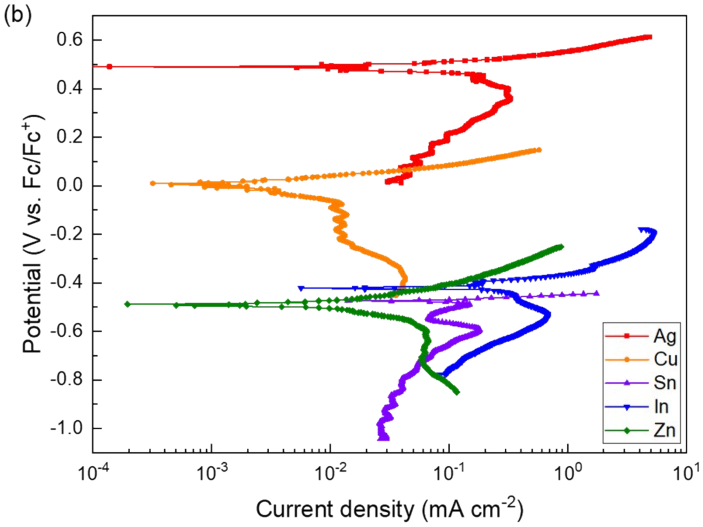


Figure S2. Potentiodynamic polarization of five metals in (a) [BMPyr] [NTf_2] and (b) [BMPyr] [Nf_2].

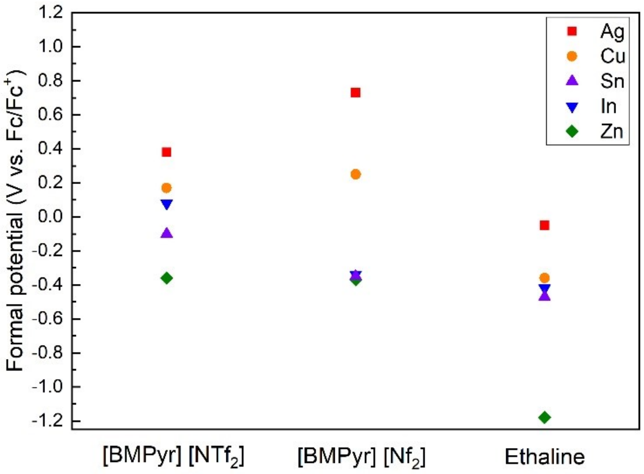


Figure S3. Formal potentials of five metals in the ionic liquids and ethaline.