

Electrochemical instability of bis(trifluoromethylsulfonyl)imide based ionic liquids as solvents in high voltage electrolytes for potassium ion batteries

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1. Experimental details

Synthesis

Non-graphitizable carbon (hard carbon, HC) was synthesized from sucrose (Rushim) by hydrothermal microwave method under 600 rpm magnetic stirring, 130°C, 30 atm. pressure. KVPO₄F (KVP) cathode materials was synthesized as described in ^{S1}.

Electrode preparation

KVP and Al₂O₃ (corundum, Sigma Aldrich, grain size was approx. 0.4 μm) powders were chosen as working electrode materials, and HC was selected as anode material to study electrochemical properties of the ionic liquids in the K⁺/K system. Composite cathodes were fabricated by mixing cathode materials powders with Super P carbon (Gelon Lib) and polyvinylidene fluoride (PVDF: Gelon Lib, HSV900, 99.5%) in the ratio 80:10:10, respectively. A slurry was formed upon the addition of N-methyl-2-pyrrolidinone (NMP: Gelon Lib, 99.9%). The anode material powder was mixed with Super P carbon (Gelon Lib) and common binder sodium carboxymethyl cellulose (Na-CMC: SigmaAldrich) in the following ratios - active material:carbon super P:Na-CMC = 80:10:10. Deionized water (Millipore Direct-Q®3UV) was used to prepare anode material slurry. The electrode slurries were spread over Al foil (Gelon Lib, 113 μm) using the Automatic Film Applicator Zehntner ZAA 2300. The obtained electrodes with the thicknesses of 150 μm were dried under vacuum at 100°C for 8 hours. The medium mass of electrode active materials was about 2-2.5 mg·cm⁻², and the electrode square was 2 cm².

Electrolyte preparation

Four ILs were studied: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BuMePyr⁺TFSI: SigmaAldrich, 98%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BuMeIm⁺TFSI: TCI chemicals, 99.99%), 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MePrPyr⁺TFSI: TCI chemicals, 99.6%) and 1-ethyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide (EtMePy⁺TFSI: TCI chemicals, 99.9%). Potassium bis(trifluoromethanesulfonyl)imide (KTFSI: SigmaAldrich, 97%) and potassium hexafluorophosphate (KPF₆: Acros organics, 99%) were dissolved in ILs to achieve the following

concentrations: (i) 0.5 M KTFSI and (ii) [0.1 M KTFSI + 0.111 M KPF₆]. In order to compare the electrochemical behavior of ILs and conventional carbonate-based electrolyte, a solution of 0.5 M KPF₆ in ethylene carbonate(EC)/propylene carbonate(PC) (SigmaAldrich, anhydrous, 99%) in the ratio 1:1 (v:v) was prepared.

Electrochemical measurements

The electrochemical properties of the electrolytes were studied in two-electrode swagelock stainless steel cells with glass-microfibre separators (Munktell Ahlstrom, 250 μm thickness) and the working volume of $\sim 100 \mu\text{L}$. The cells were assembled in an MBraun MB-200B glove box under argon atmosphere ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 0.1 \text{ ppm}$). Aluminum current collector corrosion, electrolyte low- and high-voltage stability were investigated using Al, Al₂O₃, KVP and HC as working electrodes in cells with metallic potassium anodes.

Cyclic voltammetry (CV) measurements were conducted in three potential ranges: 0.5–2.5 V, 2–5.1 V and 2.5–5.5 V vs. K⁺/K at $50 \mu\text{V}\cdot\text{s}^{-1}$ scan rate. Electrochemical impedance spectroscopy (EIS) measurements were performed in potassium symmetric cells. Impedance spectra were registered at open circuit potential in the frequency range 100 kHz to 10 MHz with alternating voltage amplitude 10 mV.

All the electrochemical measurements were performed using Biologic VMP3 potentiostat/galvanostat.

2. Additional experimental data

Cycling voltammetry

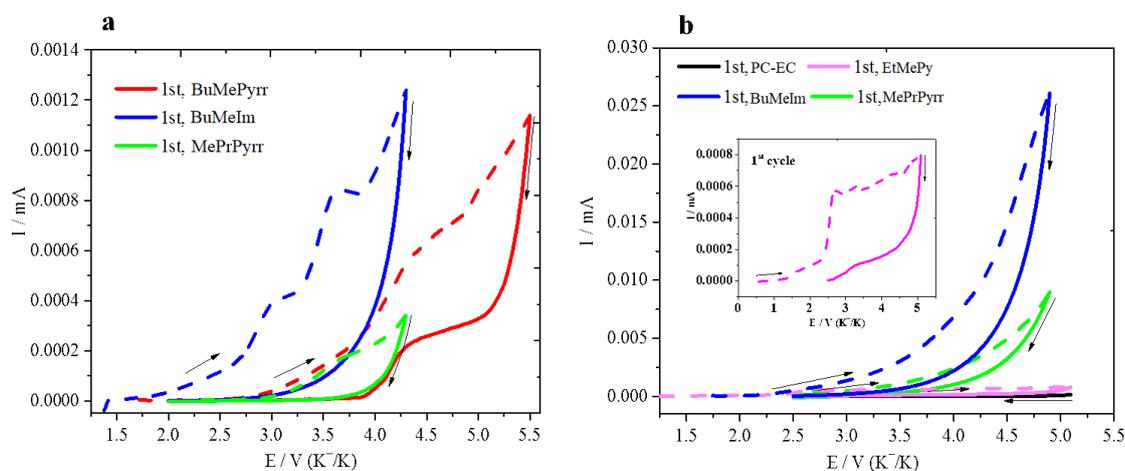


Figure S1 (a) CVs (1st cycles) in two electrode Al|K cells in 0.5 M KTFSI/BuMePyrrTFSI, BuMeImTFSI and MePrPyrrTFSI electrolytes at $100 \mu\text{V}\cdot\text{s}^{-1}$; (b) CVs (1st cycles) in two electrode Al|K cells in [0.1 M KTFSI+0.111 M KPF₆]/BuMeImTFSI, MePrPyrrTFSI, EtMePyTFSI and PC-EC electrolytes at $100 \mu\text{V}\cdot\text{s}^{-1}$. The inset in (b) shows the enlarged part of CV in EtMePyTFSI-based electrolyte.

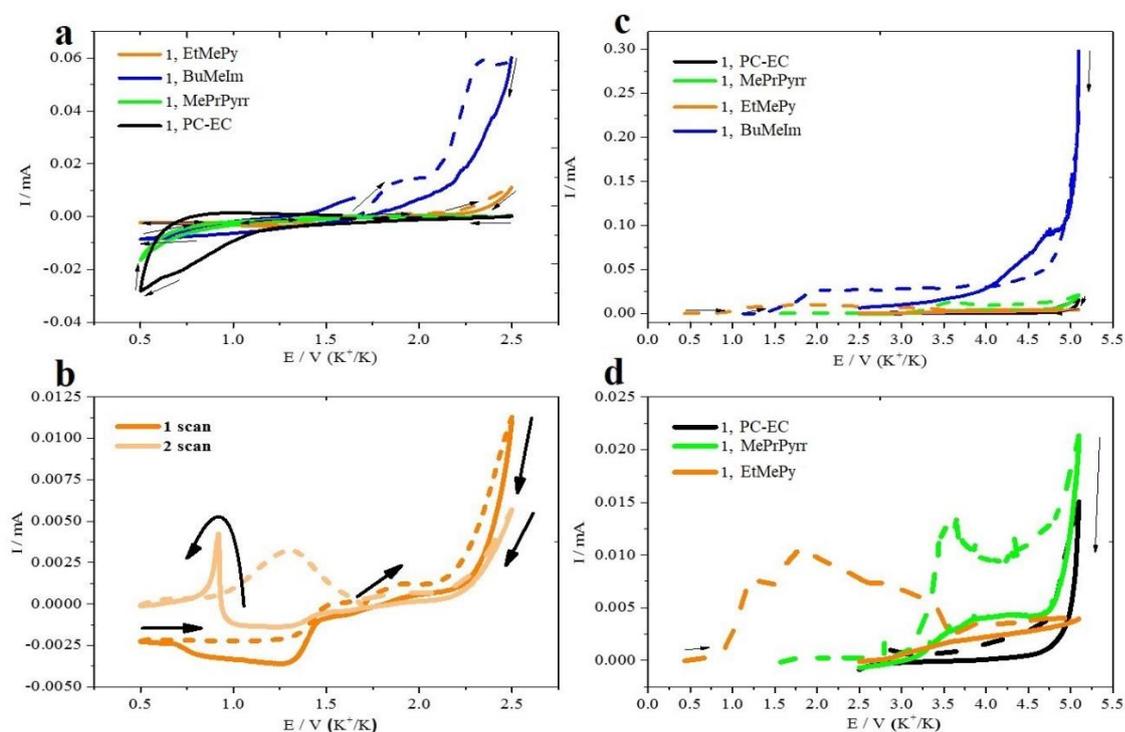


Figure S2 CVs in two electrode Al₂O₃|K cells in [0.1 M KTFSI+0.111 M KPF₆]/BuMeImTFSI, MePrPyrrTFSI, EtMePyTFSI and PC-EC electrolytes at $100 \mu\text{V}\cdot\text{s}^{-1}$: (a) CVs of 1st scans in 0.5–2.5 V range; (b) CVs of 1st and 2nd scans in EtMePyTFSI-based electrolyte; (c) CVs of 1st scans in 2.5–5.5 V range and -0.01 to 0.35 mA (scan started from OCV); (d) CVs of 1st scans in 2.5–5.5 V range and -0.0025 to 0.025 mA.

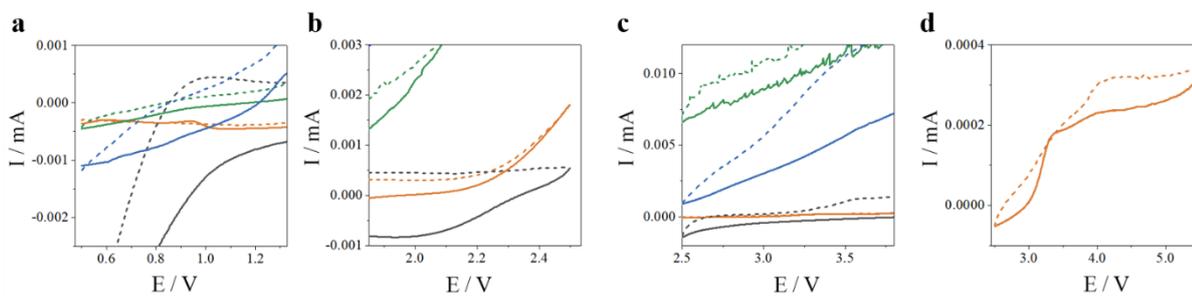


Figure S3 Enlarged parts of CVs (10th cycles) in two electrode Al₂O₃|K cells in [0.1 M KTFSI+0.111 M KPF₆]/BuMeImTFSI, MePrPyrrTFSI, EtMePyTFSI and PC-EC electrolytes at 100 μV·s⁻¹: 0.5–2.5 V vs. K⁺/K range: (a) 0.45–1.35 V and (b) 1.6–2.55 V; 2.5–5.5 V vs. K⁺/K range: (c) 2.5–3.55 V and (d) CV of BuMeImTFSI-based electrolyte.

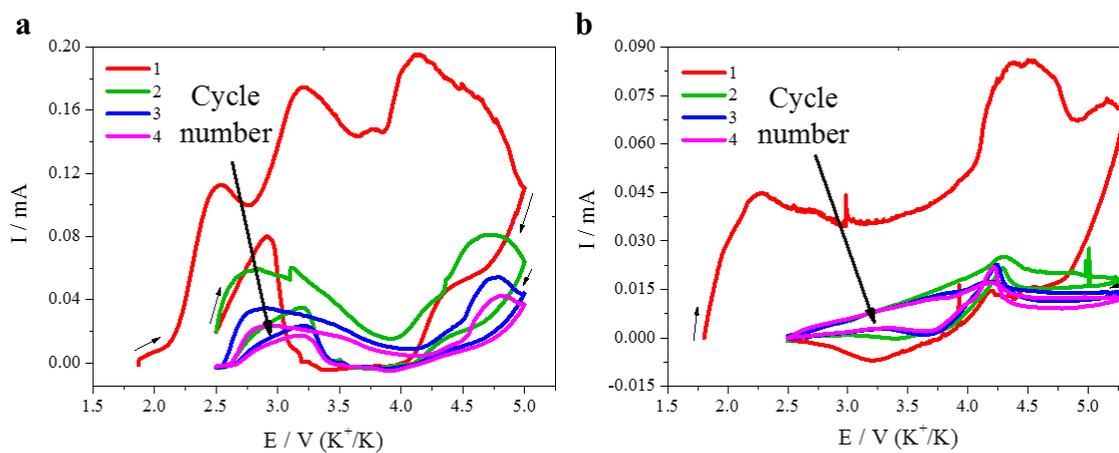


Figure S4 CVs of KVPO₄F electrode in KVP|K cell with (a) [0.1 M KTFSI+0.111 M KPF₆]/ EtMePyTFSI electrolyte and (b) [0.1 M KTFSI+0.111 M KPF₆]/BuMeImTFSI at 100 μV·s⁻¹.

Electrochemical Impedance Spectroscopy

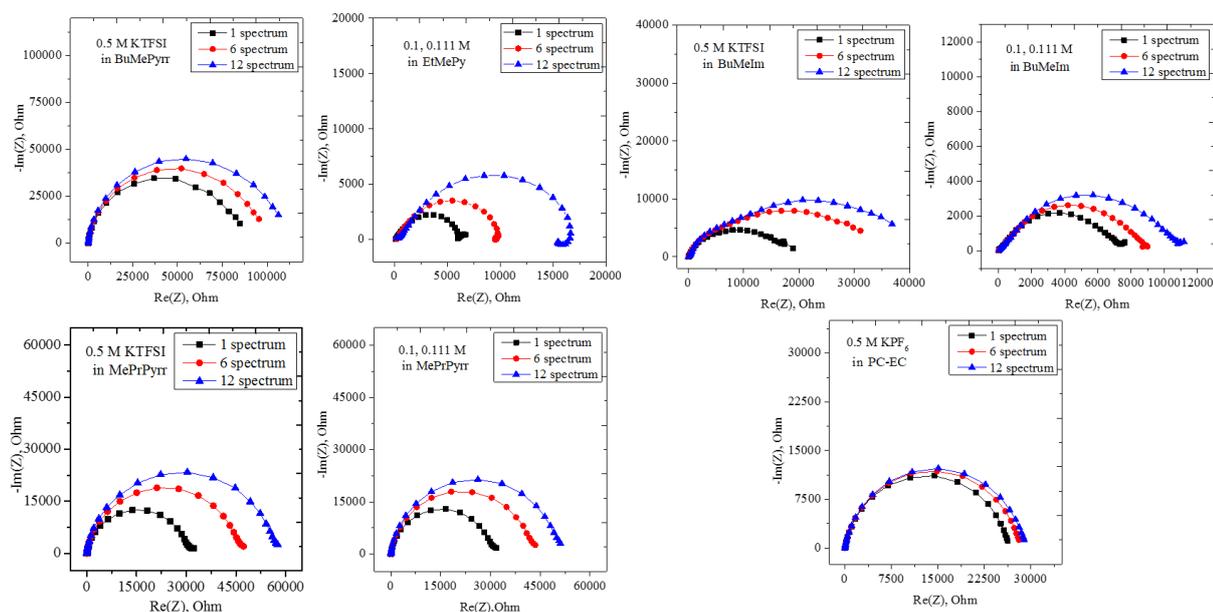


Figure S5 1st, 6th and 12th impedance spectra of 0.5 M KTFSI/BuMePyrrTFSI, 0.5 M KTFSI/ EtMePyTFSI, 0.5 M KTFSI/MePrPyrrTFSI, 0.1 M KTFSI, 0.111 M KPF₆/MePrPyrrTFSI, 0.5 M KTFSI/BuMeImTFSI, 0.1 M KTFSI, 0.111 M KPF₆/BuMeImTFSI, 0.5 M KPF₆/PC-EC = 1:1 (v/v) (from up to bottom, from left to right, respectively).

XRD and SEM characterization

The crystal structure of KVPO₄F was studied by powder X-ray diffraction analysis on a Bruker D8 Advance diffractometer with a reflection geometry, Cu K_α radiation. The morphology of the electrode materials powders was studied by scanning electron microscopy (SEM, JEOL JSM-6490LV with 30 kV accelerating voltage).

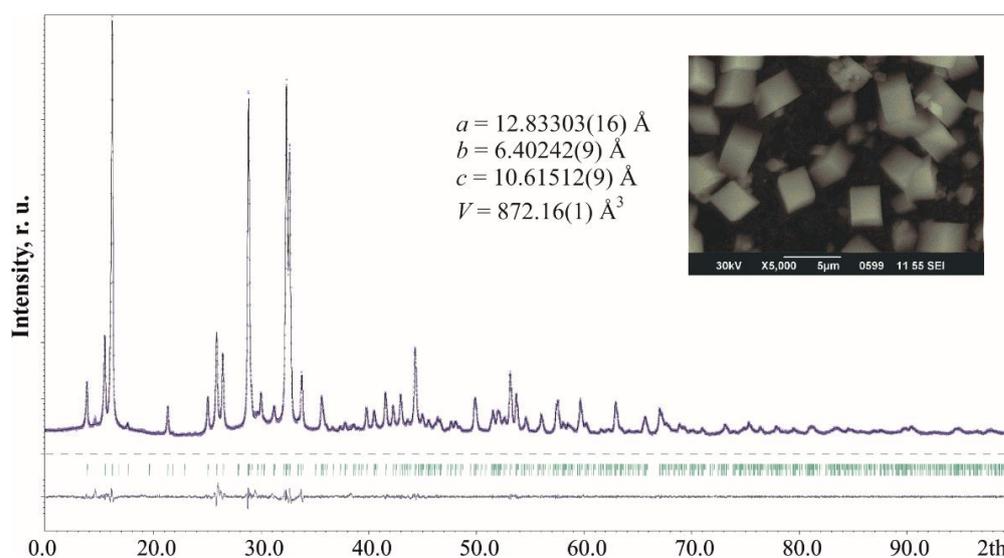


Figure S6 Experimental, calculated and difference X-ray powder diffraction profiles after Rietveld refinement of the KVPO₄F cathode material. The inset shows SEM image of KVPO₄F powder.

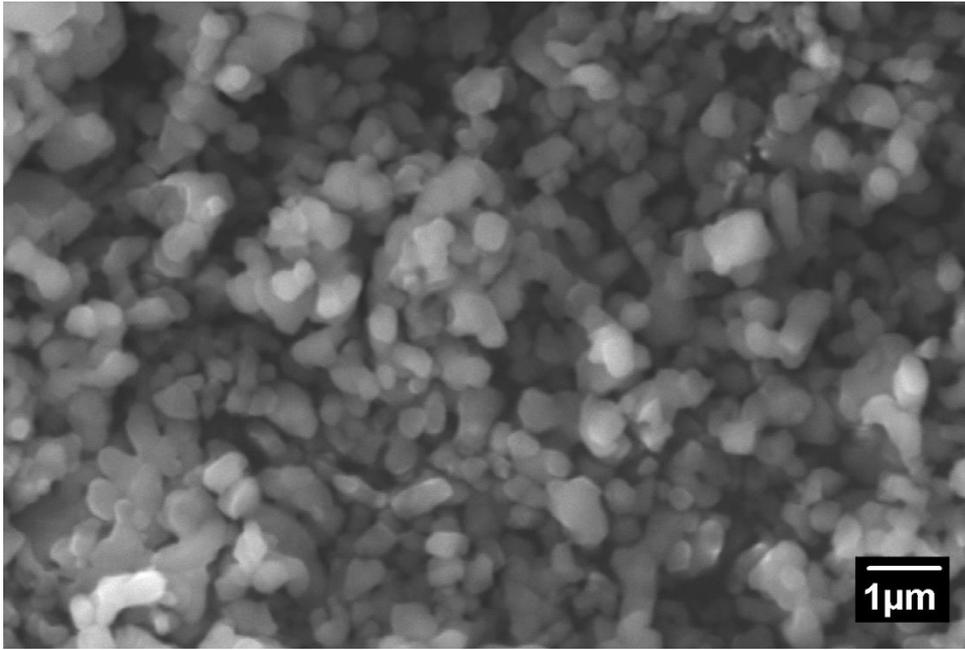


Figure S7 SEM image of α -Al₂O₃ powder.

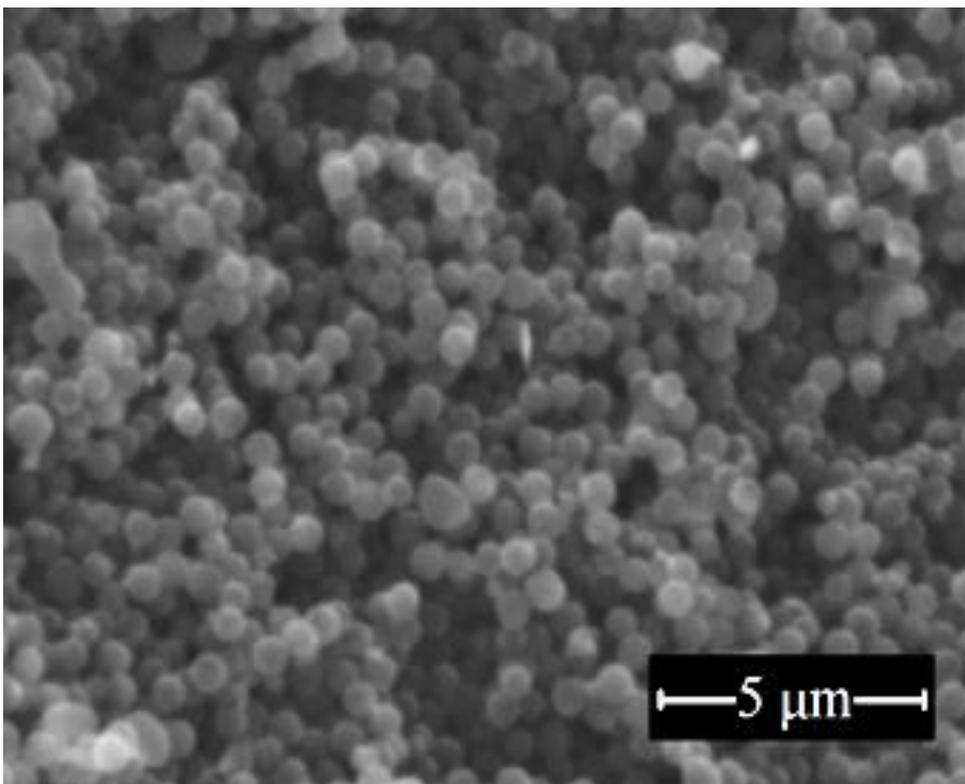


Figure S8 SEM image of hard carbon powder.

References

- S1 S. S. Fedotov, N. R. Khasanova, A. S. Samarin, O. A. Drozhzhin, D. Batuk, O. M. Karakulina, J. Hadermann, A. M. Abakumov and E. V Antipov, *Chem. Mater.*, 2016, **28**, 411.