Electronic Supplementary Information

Effect of the electrolyte on the K-metal batteries

Justine Touja,[a,b] Phuong Nam Le Pham,[a,c] Nicolas Louvain,[a,b,c] Laure Monconduit,[a,b,c,*] Lorenzo Stievano [a,b,c,*]

[a.] *ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France.*
[b.] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, Hub de l'Energie, Amiens, France.*
[c.] *ALISTORE-European Research Institute, FR CNRS 3104, Hub de l'Energie, Amiens, France.*

Experimental:

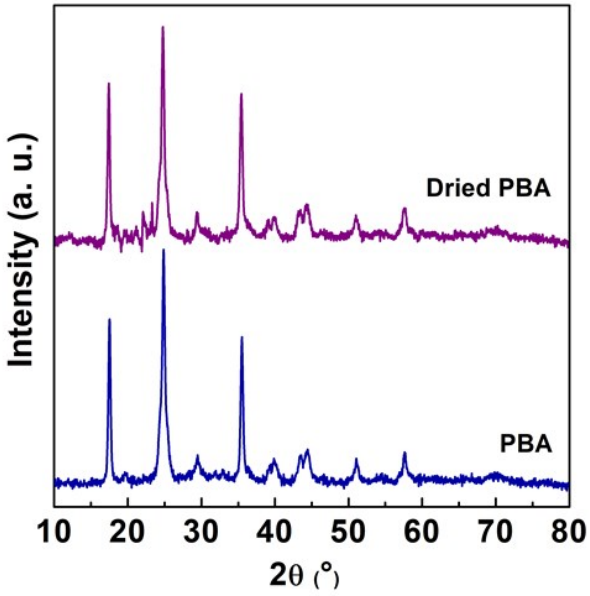
Materials: KFSI (purity 99.9 %, Solvionic) and KTFSI (purity 99.5 %, Solvionic) salts were used as received. The DME (99.5 %, anhydrous) solvent was purchased from Sigma Aldrich, and was used without any purification. The electrolytes were prepared by dissolving the desired amount of salt in the solvent, and were stirred overnight in an argon-filled glovebox (MBraun, H2O < 0.5 ppm, O2 < 0.5 ppm).

Materials characterization: X-ray diffraction (XRD) measurements were performed on a PANalytical X'Pert Pro MPD diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) and a step size of 0.033° between 10° and 80°. Optical microscopy images were acquired with a Bresser LCD microscope (40X) located inside an Ar filled glovebox to protect the analysed sample from decomposition.

Synthesis of Prussian blue analogue (PBA) cathode materials: $K_{1.73}Mn_{2/3}Fe_{1/3}[Fe(CN)_6]\cdot nH_2O$ was prepared by a precipitation method: $K_4[Fe(CN)_6]\cdot 3H_2O$ as well as appropriate proportions of $FeSO_4\cdot 7H_2O$ and $MnSO_4\cdot H_2O$ were dissolved in 100 mL and 80 mL of saturated KCl solution, respectively. The latter solution was slowly dropped into the former one and the mixture was stirred at 60°C for 24h. The obtained precipitate was centrifuged and washed with deionized water five times and twice with ethanol, before being dried under vacuum. An additional drying (100°C overnight) were realized just before the electrode formulation and XRD to be sure that no residual water still remains in the powder. The XRD patterns are presented in Fig. S1 with the lattice parameters of PBA before and after this thermal step. Not only the synthesized PBA is pure but no obvious change occurs after drying which proves the structural integrity of the material.

Electrochemical measurements: The PBA electrodes were formulated by mixing PBA powder with Super P (Alfa Aesar) and polyvinylidene fluoride (PVdF, Solef® 5130) with a weight ratio of 60/30/10, for one hour using a planetary low energy ball milling. The slurry was casted on an aluminum foil, dried under air exposure, punched with a diameter of 1.27 cm and dried overnight at 80°C under vacuum before use. Coin cells (CR2032, stainless steel 304L) were assembled in the glovebox, using K metal (Sigma Aldrich) as working, and counter-electrodes for the symmetric cells with a tri-layer polypropylene polyethylene membrane (Celgard 2325) as separator. For the linear sweep voltammetry (LSV) and the half-cells, CR2032 type coin cells (stainless steel 316L) were used, with K metal as counter-electrode and a glass fiber separator (Whatman GF/D) soaked with 100 µL of the electrolyte. All these electrochemical

experiments were performed using a MPG2 (Biologic) multi-channel potentiostat. The electrochemical impedance spectroscopy of the K|K cells was measured on a VSP (Biologic) potentiostat between 1 MHz and 10 mHz with an amplitude of 10 mV.



	PBA	Dried PBA
a (Å)	10.10401	10.10021
b (Å)	10.10578	10.10011
c (Å)	10.10666	10.10487

Fig. S1. XRD patterns and lattice parameters of PBA before and after drying under vacuum

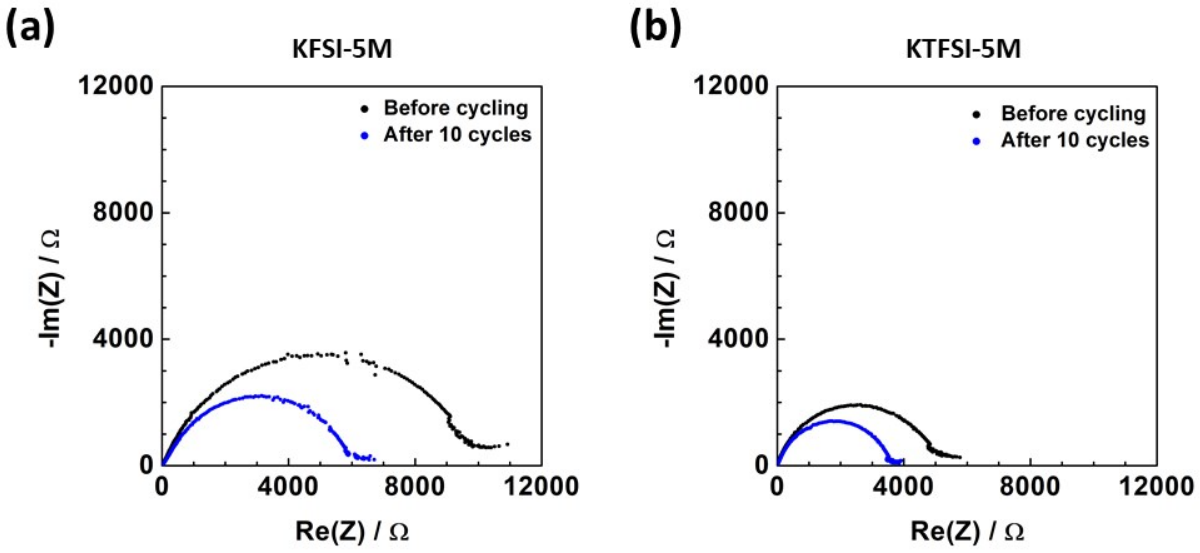


Fig. S2. Nyquist plots of the K|K cells with KFSI-5M (a) and KTFSI-5M (b) before cycling and after 10 cycles of plating/stripping at 0.025 µA.cm^{-2}

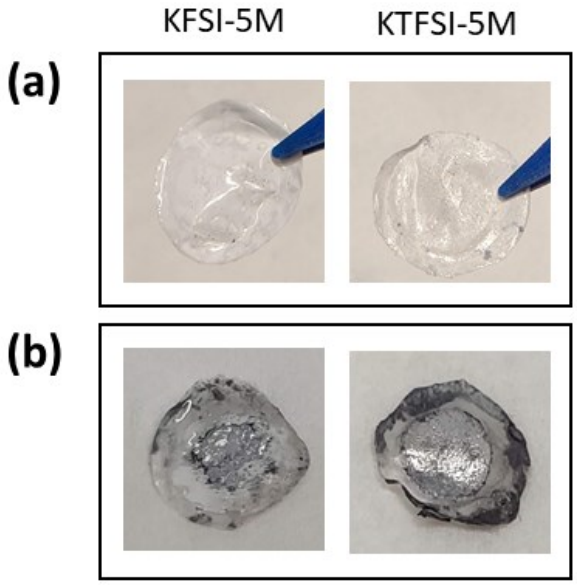


Fig. S3. Photographs of the separators after cycling at 0.025 mA.cm^{-2} (a) and 1 mA.cm^{-2} (b) with KFSI-5M (left) or KTFSI-5M (right)

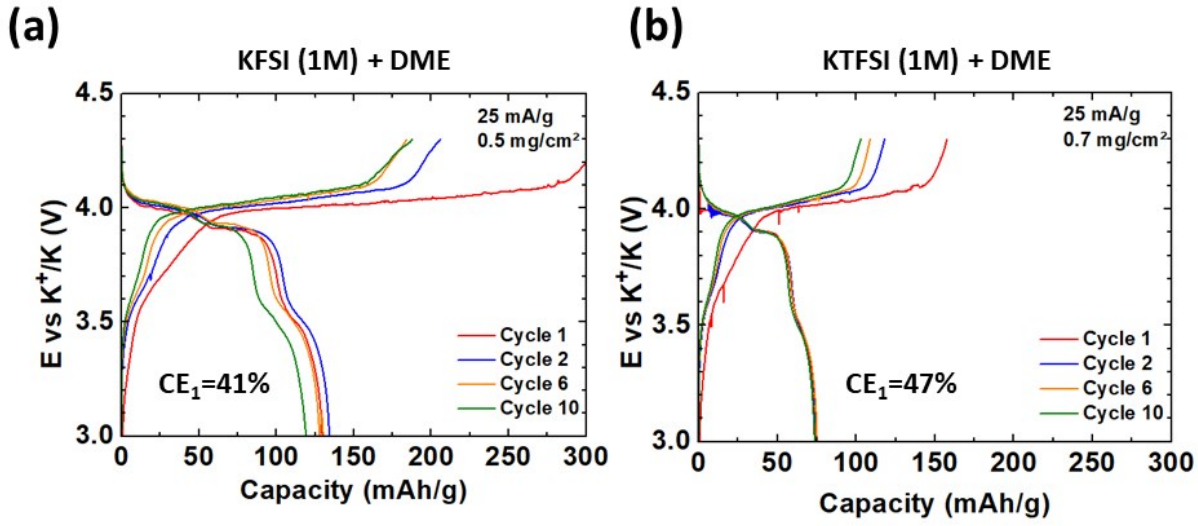


Fig. S4. Galvanostatic profiles of PBA with KFSI (1M) + DME (a) and KTFSI (1M) + DME (b) recorded at 25 mA/g between 3.0 and 4.3 V

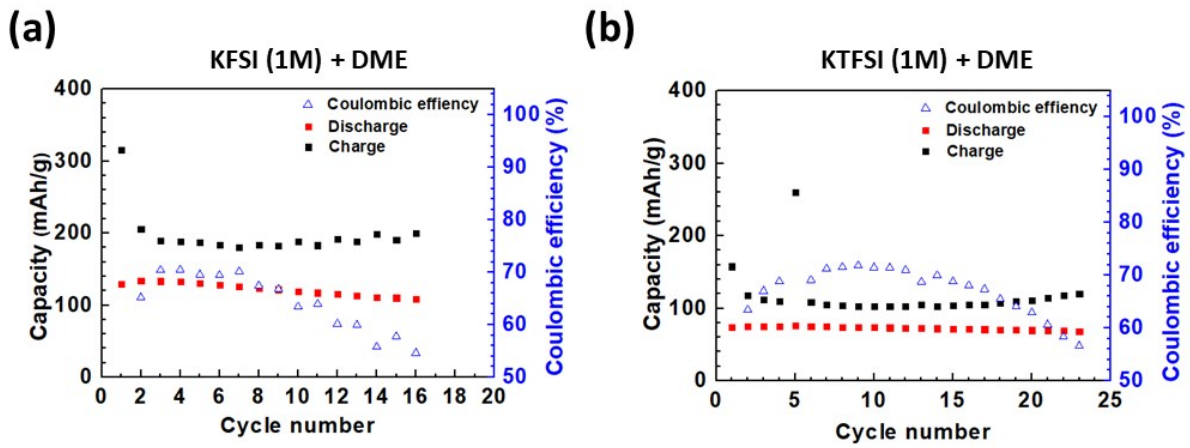


Fig. S5. Evolution of the capacity of PBA during galvanostatic cycling with KFSI (1M) + DME (a) and KTFSI (1M) + DME (b)a