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## Effect of the electrolyte on the K-metal batteries

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**The comparison of different electrolytes showed that both salt concentration and anion are key parameters for controlling the performance of K-metal batteries. Among the different tested electrolytes, 5 M KTFSI in DME exhibits the best stability at high potential and good performance in K|Prussian blue cells.**

To meet the demand for high energy density batteries, alternative systems beyond Li-ion batteries (LIBs) have to be developed. Several reasons make potassium-based batteries a perfect alternative to LIBs for large-scale energy storage applications. First, the widespread availability of potassium makes it approximately six times cheaper than lithium, and leads to cheaper precursors and salts. The electrochemical properties of the  $K^+/K$  redox couple are attractive, especially because the redox potential of  $K^+/K$  in organic solvents is lower than that of  $Li^+/Li$ , which can lead to a large potential window when associated with a high voltage cathode and thus high energy densities.<sup>1</sup> Moreover, in carbonate-based electrolytes,  $K^+$  has the highest ion mobility, ion conductivity and ion transport number among alkaline cations ( $Li^+$ ,  $Na^+$ ,  $K^+$ ). Finally, a recent study on existing commercial cell architectures and up-to-date manufacturing know-how concluded that potassium batteries are capable of achieving 78 % of the energy density of LIBs.<sup>2</sup>

Renewed design of electrochemical cells using metal negative electrodes is presently among the most promising paths to reach higher energy density batteries. In the case of lithium metal, by far the most studied system nowadays, the main issue is the uneven deposition of Li during charge that results in the

detrimental growth of dendrites.<sup>3</sup> Their formation promotes the increase of the exposed metal surface favouring the continuous decomposition of the electrolyte and the growth of the solid-electrolyte interphase (SEI), and thus a progressive loss of active metal during cycling. The same issues are observed and even enhanced when using potassium metal electrodes.<sup>4</sup> In fact, the reactivity of potassium with the electrolyte is higher, and often influences the performance of the positive electrode when the latter is tested in half cells.<sup>5,6</sup> To counter this high reactivity and stabilize the metallic electrode, some solutions have been proposed.<sup>7-9</sup>

One of the strategies to limit dendrite growth in metal anodes is using highly concentrated electrolytes. These contain fewer free solvent molecules and thus form thinner SEI, improving the cycling stability, as it has been observed for both  $Li^{10,11}$  and  $Na^{12}$ . Highly concentrated potassium electrolytes have also been investigated, for instance with potassium bis(fluorosulfonyl)imide (KFSI) dissolved in ether solvents, for graphite electrodes<sup>13,14</sup> and positive electrodes such as Prussian blue analogues (PBA).<sup>15,16</sup> Concentrated KFSI in 1,2-dimethoxyethane (DME) electrolytes, as for Li and Na, seem to prevent the corrosion of the aluminium current collector, increasing the oxidation stability up to 5 V vs.  $K^+/K$  and allowing the stable and reversible plating/stripping of potassium metal with an uniform and stable SEI.<sup>16,15</sup>

Herein a pioneer study is presented on the effect of electrolyte concentration and of the salt anion on the performance of a K-metal cell using four electrolytes with KFSI or KTFSI at 1 or 5 moles per litre of solvent (named 1M or 5M) dissolved in DME. These electrolytes will be referred to as KFSI-1M, KFSI-5M, KTFSI-1M and KTFSI-5M. Their respective impacts on the stability at high potential in the presence of Al current collectors, on the potassium plating/stripping efficiency and on the performance of a cell built with the PBA  $K_{1.73}Mn_{2/3}Fe_{1/3}[Fe(CN)_6]nH_2O$  as the positive electrode is evaluated. This type of PBA is similar to that proposed as cathode material in aqueous batteries,<sup>17</sup> and is used here as a

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benchmark cathode. A full characterisation of this material will be the object of a forthcoming paper.

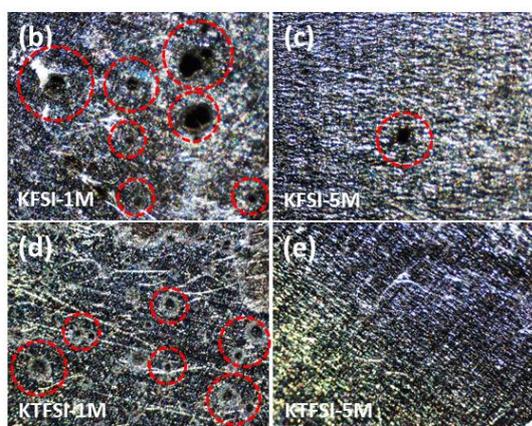
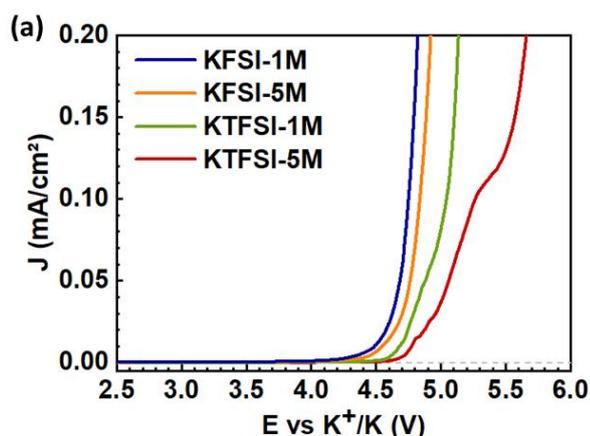
The stability at high voltage for each electrolyte was studied by linear sweep voltammetry (LSV) in coin cells built with a potassium negative electrode and an aluminium foil as the positive electrode to compare the influence of both anions and electrolytes concentrations on the aluminium corrosion (Figure 1). It is important to note that, in lithium batteries, where the electrolytes are usually based on lithium hexafluorophosphate ( $\text{LiPF}_6$ ),  $\text{PF}_6^-$  is known to protect the aluminium current collector of the positive electrode by forming an insoluble passivation layer, preserving the electrode from excessive corrosion during cycling, whereas  $\text{FSI}^-$  does not lead to such a favourable feature.<sup>18</sup> In potassium batteries, the use of KFSI-based electrolytes has the advantage of reducing the large first cycle irreversible capacities obtained with  $\text{KPF}_6$ -based ones, but brings as a drawback the loss of the interesting passivation ability of  $\text{PF}_6^-$ .<sup>19</sup>

The LSV measurements were performed with the four electrolytes at a scan rate of  $0.1 \text{ mV s}^{-1}$  up to 6 V vs.  $\text{K}^+/\text{K}$ . The anodic current increases suddenly for KFSI-1M from 4.2 V, which confirms its limited stability at high potential in the presence of aluminium (Figure 1a). With the highly concentrated electrolyte (KFSI-5M), the electrolyte decomposition or the aluminium corrosion is slightly delayed as

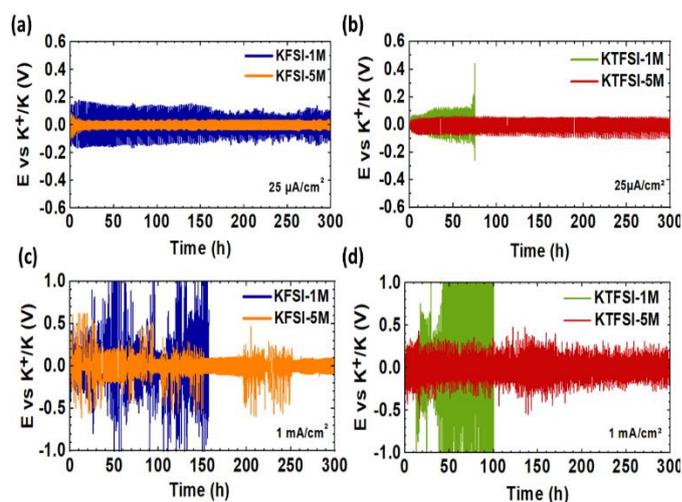
the anodic current increases only starting from 4.4 V. Changing from KFSI to KTFSI has a more important impact on the LSV. The voltage stability window is enhanced, since the current increase starts at 4.6 V for KTFSI-1M and at 4.7 V for KTFSI-5M, in agreement with previous observations.<sup>20</sup> Note that the first current raise occurring during LSV with both KTFSI-based electrolytes could be also due to the oxidation of  $\text{TFSI}^-$  anion, as previously observed in lithium systems.<sup>21</sup> The surface of the Al current collectors after the LSV (Fig. 1b-e) shows several pits when low concentrated electrolytes are used, and very few or no pits when employing highly concentrated electrolytes. This result indicates that by increasing the concentration, the corrosion at the aluminium current collector is reduced.

In summary, the stability of highly concentrated electrolytes, and especially of that based on the KTFSI salt, observed high potential might enable high energy batteries obtained by coupling new cathode materials working at high potential with K metal anodes.

The plating/stripping stability of potassium metal in these electrolytes was compared in symmetric K|K cells at different current densities, namely  $0.025 \text{ mA cm}^{-2}$  and  $1.00 \text{ mA cm}^{-2}$ . Figures 2a and 2b show the K plating/stripping voltage profiles obtained at  $0.025 \text{ mA cm}^{-2}$  with KFSI-based electrolytes and KTFSI ones, respectively. At low current density, the cell using KFSI-1M has a stable overpotential near 0.1 V for 300 h whereas with KTFSI-1M, the polarization increases rapidly after 50 h, reaching 0.5 V. A sharp increase of potential like this one has been proven to be due to the growth of dendrites which can short circuit the batteries.<sup>22</sup> In these conditions, the cells with the highly concentrated electrolytes present a lower polarization than the ones with the low concentrated electrolytes. However, the overpotential measured for KFSI-5M decreases from 800 mV to 300 mV within the ten first cycles, whereas the one for KTFSI-5M remains constant for all the experiment. The reaction between the K-metal and the electrolytes leading to different nature of SEI can explain this difference.<sup>5</sup> The electrochemical impedance spectroscopy (EIS) measured on the symmetrical cells before cycling, show that the



**Figure 1.** Linear sweep voltammetry of K-metal vs Al with the four electrolytes (a). Optical microscopy images (40X) of the Al current collector after the LSV of KFSI-1M (b), KFSI-5M (c), KTFSI-1M (d) and KTFSI-5M (e)

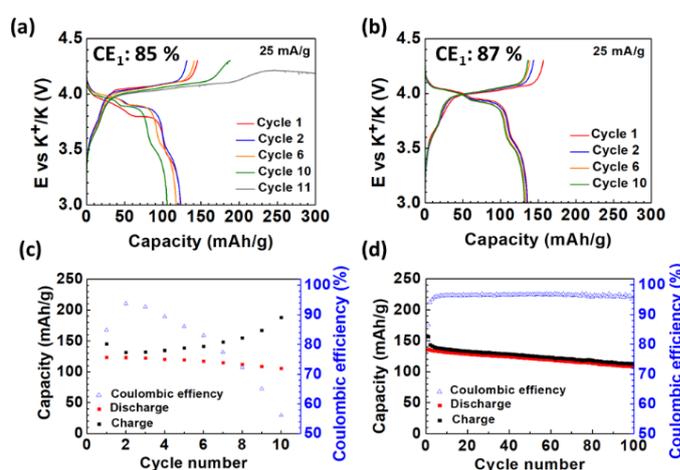


**Figure 2.** K-metal plating/stripping curves of K|K symmetric cells with KFSI-1M and KFSI-5M and KTFSI-1M and KTFSI-5M at a current density of  $25 \mu\text{A/cm}^2$  (a,b) and  $1 \text{ mA/cm}^2$  (c,d)

global resistance of the system is lower with KTFSI-5M than with KFSI-5M (Fig. S2). This is in agreement with the higher polarization of the K-metal plating/stripping with the latter electrolyte for the first cycle. The chemically formed SEI changes with the electrolyte nature and is then more resistive with the KFSI-based electrolyte than with the KTFSI-based one. After 10 cycles, the impedance decreases in both cases but remains nearly twice higher for KFSI-5M. Both highly concentrated KFSI and KTFSI-based electrolytes are, however, very stable for 300 h revealing that no, or at least fewer, dendrites are formed with these electrolytes. No colour change of the separator was observed after cycling for both 5M electrolytes (Fig. S3a). It means that neither the degradation of the salt nor the dendrites growth through the separators can be observed for low current density, as suggested by the K metal plating/stripping electrochemical measurements (Fig. 2a,b).

At a higher current density, *i.e.*,  $1 \text{ mA cm}^{-2}$ , (Fig. 2c,d) the plating/stripping curves with both 1 M-electrolytes show poor stability, since the overpotential is higher than 1 V after few hours. However, although KFSI-5M does not improve the overpotential stability (Fig. 2c), the overpotential of the cell using KTFSI-5M remains stable for 300 h around 400 mV (Fig. 2d). The use of concentrated KTFSI instead of KFSI seems to improve the stability of the plating/stripping of potassium metal, especially at high current densities. After opening the batteries, the separator of the KFSI-5M cell was partially covered with K-metal whereas the one of KTFSI-5M cell was fully covered at the location of the metallic electrode (Fig. S3b). This also suggests that the plating of K-metal is more homogeneous with KTFSI-5M than with KFSI-5M. The reactions between the potassium and the electrolyte may have a lower impact on the galvanostatic measurement of a half-cell with KTFSI-5M.

The electrolytes were finally benchmarked using PBA cathodes ( $\text{K}_{1.73}\text{Mn}_{2/3}\text{Fe}_{1/3}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ) between 4.3 and 3.0 V vs.  $\text{K}^+/\text{K}$  at a current rate of  $25 \text{ mA g}^{-1}$ . The galvanostatic curves for  $\text{K}|\text{PBA}$  cells using either low or highly concentrated electrolytes are presented in Fig. S4 and Fig. 3a,b, respectively. The average shape of the galvanostatic curves is similar for the four electrolytes, and is consistent with that observed by Jiang *et al.* in different electrolyte systems.<sup>17</sup> The initial coulombic efficiency (CE) is clearly improved for the highly concentrated electrolytes. For KFSI-1M, the first charge capacity is surprisingly high ( $316 \text{ mA h g}^{-1}$ ) compared to the first charge of KFSI-5M ( $145 \text{ mA h g}^{-1}$ ) but the CE is stable only for five cycles before dropping (Fig. S5a). Even though the initial CE is high for KFSI-5M, with a value of 85%, it drastically drops after a few cycles (Fig. 3c) due to the steady increase of the charge capacity after four cycles and the irreversible cell failure after ten cycles. Such a behaviour, already reported for KFSI (1 M) in EC/DEC, results from the formation of a non-conductive passivation layer for  $\text{K}^+$  ions on the potassium metal, as well as from the growth of potassium dendrites leading to short-circuits.<sup>23</sup> This behaviour is consistent with the plating/stripping results reported above. Moreover, the instability above 4 V of the KFSI-based electrolytes observed by LSV, due to parasitic oxidation reactions such as electrolyte decomposition and/or Al



**Figure 3.** Galvanostatic profiles and long-term cycling evolution of PBA with KFSI-5M (a,c) and KTFSI-5M (b,d) recorded at  $25 \text{ mA/g}$  between 3.0 and 4.3 V

corrosion, could also explain the observed coulombic efficiency drops.

For the KTFSI-based electrolytes, the increase in salt concentration allows higher specific capacities, and the long-term cycling highlights the better stability and reversibility of the reactions, in comparison with KTFSI-1M (Fig. 3d, Fig. S5b). This is probably due to the thinner and more inorganic SEI formed during the galvanostatic experiment with concentrated electrolytes.<sup>24</sup>

On the other hand the higher polarization observed in the first cycle with KFSI-5M electrolyte could be due to the SEI formed on the K-metal. Indeed, the plating/stripping and the EIS measurements showed that the SEI is more resistive with the highly concentrated KFSI-based electrolyte than with the KTFSI-based one, especially for the first cycles. The reactivity of the K-metal with the electrolyte has an impact on the electrochemical performance of the half-cells as suggested.

The anion used in the electrolyte plays also an important role for the cycling stability of the cathode. Indeed, for both 5 M KFSI and KTFSI in DME, the capacities are quite the same for the first cycles but the use of TFSI instead of FSI enhances the capacity retention, which remains at  $110 \text{ mA h g}^{-1}$  after 100 cycles (*i.e.* 72 % of the initial capacity), as well as the CE (96 %). The electrochemical performance of PBA was shown to be controlled by different parameters such as crystallinity, defects or lattice water content,<sup>25,26</sup> which can explain the slight differences between the results shown here and those previously obtained with highly concentrated KFSI electrolytes.<sup>15</sup>

In conclusion, both the salt and its concentration in the electrolyte have a strong impact on the electrochemical stability of potassium metal batteries. By increasing the concentration from 1 M to 5 M in both KFSI and KTFSI in DME electrolytes, the Al current collector corrosion is delayed in potential, allowing the use of high voltage cathodes. Spectroscopic analyses of the

Al current collector surface are required to get deeper insight on its behaviour with respect to electrolyte salt and concentration. Moreover, concentrated electrolytes improve the stability of potassium metal plating/stripping, especially for the KTFSI-5M system, demonstrating the crucial role of the salt anion on the SEI formation. The SEI formed with KTFSI is likely more favourable for the plating/stripping of potassium, reducing parasitic reactions and dendrite growth. These results suggest that potassium metal electrode is more stable with KTFSI-5M, less impacting the electrochemical performance of the positive electrode. This assumption is confirmed here in K|PBA cells, showing enhanced capacity as well as CE performance after 100 cycles with the highly concentrated KTFSI electrolyte. Further studies are ongoing to analyse and compare the SEI formed with these different electrolytes, and to better understand their impact on potassium metal plating/stripping as well as on the K|PBA battery performance.

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### Conflicts of interest

There are no conflicts to declare.

### Notes and references

- 1 K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura and S. Komaba, *Chem. Rec.*, 2018, 459–479.
- 2 A. Eftekhari, *ACS Sustain. Chem. Eng.*, 2019, 7, 3684–3687.
- 3 X.-B. Cheng, R. Zhang, C.-Z. Zhao and Q. Zhang, *Chem. Rev.*, 2017, 117, 10403–10473.
- 4 C. Wei, Y. Tao, H. Fei, Y. An, Y. Tian, J. Feng and Y. Qian, *Energy Storage Mater.*, 2020, 30, 206–227.
- 5 L. Madec, V. Gabaudan, G. Gachot, L. Stievano, L. Monconduit and H. Martinez, *ACS Appl. Mater. Interfaces*, 2018, 10, 34116–34122.
- 6 J. Steiger, G. Richter, M. Wenk, D. Kramer and R. Mönig, *Electrochem. commun.*, 2015, 50, 11–14.
- 7 T. Hosaka, S. Muratsubaki, K. Kubota, H. Onuma and S. Komaba, *J. Phys. Chem. Lett.*, 2019, 10, 3296–3300.
- 8 H. Wang, D. Yu, X. Wang, Z. Niu, M. Chen, L. Cheng, W. Zhou and L. Guo, *Angew. Chemie - Int. Ed.*, 2019, 58, 16451–16455.
- 9 P. Liu and D. Mitlin, *Acc. Chem. Res.*, 2020, 53, 1161–1175.
- 10 Y. Yamada, J. Wang, S. Ko, E. Watanabe and A. Yamada, *Nat. Energy*, , DOI:10.1038/s41560-019-0336-z.
- 11 J. Zheng, J. A. Lochala, A. Kwok, Z. D. Deng and J. Xiao, *Adv. Sci.*, 2017, 4, 1–19.
- 12 J. Lee, Y. Lee, J. Lee, S. M. Lee, J. H. Choi, H. Kim, M. S. Kwon, K. Kang, K. T. Lee and N. S. Choi, *ACS Appl. Mater. Interfaces*, 2017, 9, 3723–3732.
- 13 L. Qin, N. Xiao, J. Zheng, Y. Lei, D. Zhai and Y. Wu, *Adv. Energy Mater.*, 2019, 9, 1902618.
- 14 X. Niu, L. Li, J. Qiu, J. Yang, J. Huang, Z. Wu, J. Zou, C. Jiang, J. Gao and L. Wang, *Solid State Ionics*, 2019, 341, 115050.
- 15 T. Hosaka, K. Kubota, H. Kojima and S. Komaba, *Chem. Commun.*, 2018, 54, 8387–8390.
- 16 N. Xiao, W. D. McCulloch and Y. Wu, *J. Am. Chem. Soc.*, 2017, 139, 9475–9478.
- 17 L. Jiang, Y. Lu, C. Zhao, L. Liu, J. Zhang, Q. Zhang, X. Shen, J. Zhao, X. Yu, H. Li, X. Huang, L. Chen and Y. S. Hu, *Nat. Energy*, 2019, 4, 495–503.
- 18 Y. Yamada, C. H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama and A. Yamada, *ChemElectroChem*, 2015, 2, 1687–1694.
- 19 L. Deng, Y. Zhang, R. Wang, M. Feng, X. Niu, L. Tan and Y. Zhu, *ACS Appl. Mater. Interfaces*, 2019, 11, 22449–22456.
- 20 X. Liu, G. A. Elia, X. Gao, B. Qin, H. Zhang and S. Passerini, *Batter. Supercaps*, 2020, 3, 261–267.
- 21 D. W. McOwen, D. M. Seo, O. Borodin, J. Vatamanu, P. D. Boyle and W. A. Henderson, *Energy Environ. Sci.*, 2014, 7, 416–426.
- 22 K. N. Wood, M. Noked and N. P. Dasgupta, *ACS Energy Lett.*, 2017, 2, 664–672.
- 23 X. Jiang, T. Zhang, L. Yang, G. Li and J. Y. Lee, *ChemElectroChem*, 2017, 4, 2237–2242.
- 24 J. Zheng, Y. Yang, X. Fan, G. Ji, X. Ji, H. Wang, S. Hou, M. R. Zachariah and C. Wang, *Energy Environ. Sci.*, 2019, 12, 615–623.
- 25 J. Chen, L. Wei, A. Mahmood, Z. Pei, Z. Zhou, X. Chen and Y. Chen, *Energy Storage Mater.*, 2020, 25, 585–612.
- 26 A. Zhou, Z. Xu, H. Gao, L. Xue, J. Li and J. B. Goodenough, *Small*, 2019, 15, 1902420.