

Stable cycling of graphite in an ionic liquid based electrolyte

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1-Ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (EMI-TFSI) has been shown to reversibly permit lithium intercalation into standard graphite when vinylene carbonate is used in small amounts as an additive.

Lithium-ion batteries show the highest energy density among the applicable chemical and electrochemical energy storage systems (up to 180 Wh kg⁻¹). For the negative electrode material graphite has preference, because of its stable cycling properties and its improved safety compared to lithium metal batteries. The fact that graphite electrodes can function is due to the use of electrolytes containing ethylene carbonate (EC). This builds up an ionically conductive film which protects against its own further reduction. As the organic carbonates are flammable, the use of such electrolytes poses a safety risk and reduces the temperature range of use.

Ionic liquids have been attracting interest for lithium and lithium-ion batteries, as they show a relatively large electrochemical¹⁻³ along with a high thermal stability^{1,2} and they possess a high conductivity.⁴ They show a much reduced flammability and a nearly non-existent vapour pressure even at elevated temperatures.⁵ In general they are not environmentally hazardous.⁶

Early attempts to cycle lithium-ion batteries using electrolytes on the basis of ionic liquids failed. The reason is that electrolyte reduction occurs at the low potential at which the intercalation of lithium into the graphite proceeds. One exception is systems based on aluminium chloride. However, these are difficult to prepare and are toxic due to AlCl₃.^{7,8} Also the deposition of lithium metal has been observed in such systems, but without examining the long term stability of the deposited metal.³ Only recently a partial lithium intercalation into graphite was obtained in AlCl₃-free systems but with only poor yield and only between 5–10 cycles.^{9,10} In one of these cases Sakaeb *et al.* used *N*-methyl-*N*-propylpiperidinium-bis(trifluoromethylsulfonyl)imide (PPI3-TFSI).⁹ In the other case Katayama *et al.* used ethylene carbonate which was added to *n*-hexyltrimethylammonium-bis(trifluoromethylsulfonyl)imide.¹⁰ Interestingly, lithium metal seems to also have a certain stability in *N*-methyl-*N*-alkylpiperidinium-TFSI^{9,11} and in quaternary ammonium salts, as cycling curves of Li/LiCoO₂ indicate.⁹ We present here the results we have obtained on the highly reversible and very stable cycling of graphite electrodes in a vinylene carbonate containing electrolyte, based on 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (EMI-TFSI).[†] The graphite used is TIMREX[®] SFG44 (Timcal SA, Bodio, Switzerland). It was tested against lithiated lithium titanium spinel Li_{4+x}Ti₅O₁₂, as lithium was avoided because of its possible reaction with the ionic liquid samples. It was also tested, in a full cell configuration, against standard LiCoO₂. The active material load was about 2–3 mg of graphite. The Li–Ti-spinel was lithiated against lithium prior to use. The graphite samples were tested against the so-obtained lithiated spinel electrodes (using an excess of ca. 300% of spinel to compensate for eventual capacity losses of the graphite material). The salts used in this study were LiTFSI and LiPF₆ (Stella, Japan). The additives tested were ethylene carbonate (EC, obtained from Merck KGaA, Darmstadt, Germany), vinylene carbonate (VC), ethylene sulfite and acrylonitrile (all obtained from Fluka, Buchs, Switzerland).

Fig. 1 shows the reduction of an EMI-TFSI – 1 M LiTFSI

electrolyte. A large plateau at about –0.75 V (+0.8 V vs. Li/Li⁺) shows the reduction of the electrolyte (probably the EMI⁺ cation) without intercalation of lithium into the graphite. (The reduction of the ionic liquid proceeds under the formation of soluble products, probably under oligomerisation¹²). Hence, no protective, electrolyte blocking but Li⁺-ion conductive layer, is formed. This is necessary for the correct functioning of a graphite anode. Also in the case of an electrolyte where 25% of EC was added, no protective film was formed but the reduction of the organic compounds was a continuous process. At the end of the reduction processes the voltage of the negative electrode dropped. This is an effect of the increasing passivation of the electrode, due to the continued reduction of the ionic liquid. When EC is replaced with 2% of acrylonitrile as an additive to EMI-TFSI – 1 M LiTFSI, the cycling curve lowers more rapidly to more negative potentials. Upon the following discharge some capacity is obtained at a potential negative to –1 V (+0.5 V vs. Li/Li⁺), which means that some lithium was intercalated reversibly into the graphite. On replacing acrylonitrile by 5% of ethylene sulfite or 10% of VC the situation still ameliorates and the cycling curves become closer to the graphite curves in a standard electrolyte. VC is known as a highly efficient film forming additive for lithium-ion battery electrolytes.¹³ Indeed, the curves obtained for VC even show the typical staging phenomena. These results show that the intercalation of lithium into graphite is possible in VC-containing and partially in ethylene sulfite- and acrylonitrile-containing EMI-TFSI-based electrolytes. The capacity which is situated at the voltage range around –0.5–0 V vs. Li_{4+x}Ti₅O₁₂ corresponds to the reduction of the additives. This results in the formation of a coherent insoluble film, protecting the electrolyte from further reduction. Upon subsequent cycling for those three systems, acrylonitrile does not show a high capacity. As in the case of ethylene sulfite, which shows capacities of up to 200 mAh g⁻¹, the capacities obtained decline rapidly. Only in the case of VC is the capacity around 350 mAh g⁻¹, *i.e.*, in the order of the standard value which is obtained for the lithiation of graphite in standard electrolytes (372 mAh g⁻¹).

As LiPF₆ is known for its good film forming properties, we used

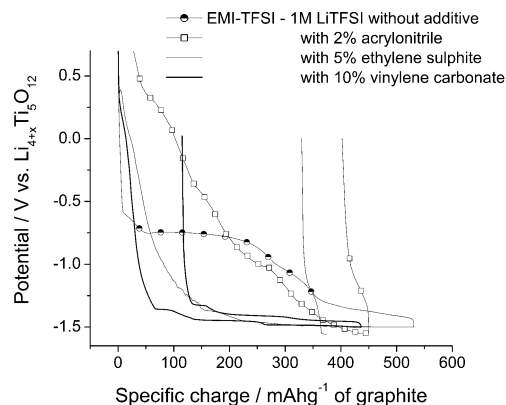


Fig. 1 Reduction of SFG44 in EMI-TFSI – 1 M LiTFSI with and without additives.

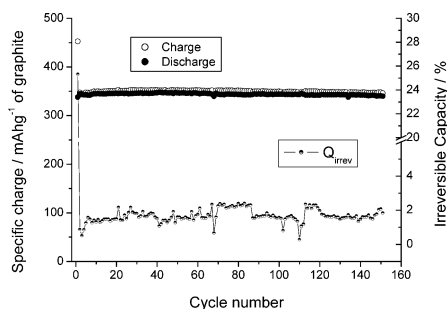


Fig. 2 Highly reversible cycling of SFG44 in EMI-TFSI – 1 M LiPF₆ – 5% VC.

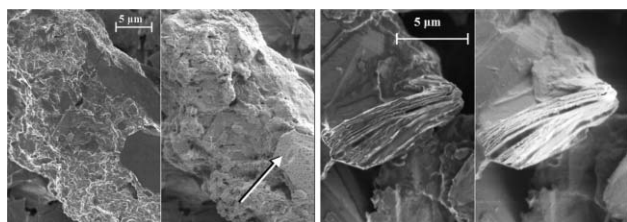


Fig. 3 SEM micrographs of SFG44 electrodes after stabilisation at 300 mV vs. Li/Li⁺ in EMI-TFSI – 1 M LiPF₆ without (left) and with 5% VC (right). In both cases the right hand images have been made in the surface sensitive secondary electron mode.

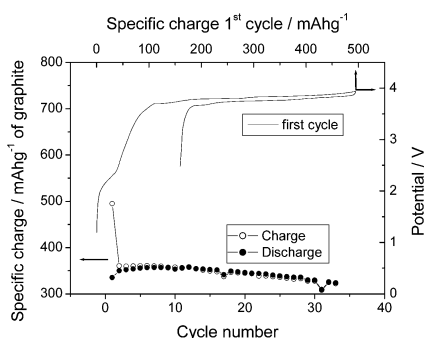


Fig. 4 Cycling of a SFG44/LiCoO₂ cell (graphite limited) in an EMI-TFSI – 1 M LiPF₆ – 5% VC electrolyte.

it as electrolyte salt in the following experiments. Fig. 2 shows the results of the cycling experiments of an SFG44 electrode in the electrolyte EMI-TFSI – 1 M LiPF₆ with 5% VC. The feasibility of the cycling of graphite in these electrolytes is clearly shown. In this electrolyte no fading is evident for up to 150 cycles, only a small capacity loss between the charge and discharge is observed (1.5–2%). This is slightly increased when compared to the classical electrolyte EC : DMC (1 : 1) – 1 M LiPF₆, where it is of the order of 0.2%. For lower concentrations of VC (2%) the capacity loss per cycle is higher (4%) and the reversible capacity lower (around 300 mAh g⁻¹). This shows that the film formed under these conditions is not yet fully stable. For only 1% of VC, cycling of graphite is no longer possible. Indeed, scanning electron microscopy (SEM, Fig. 3) shows that a homogeneous thin protective film is formed in the case of the 5% VC-containing electrolyte. However, loose aggregates of reduction products together with uncovered graphite particles (arrow) are found in the case of the VC-free electrolyte. This is, to our best knowledge, the first time that a passivation film on graphite has been identified in an ionic liquid electrolyte.

Fig. 4 finally presents the result of a full cell SFG44 – LiCoO₂, in EMI-TFSI – 1 M LiPF₆ – 5% VC. The cell is balanced with a two-fold excess of LiCoO₂ in order to account for the irreversible capacity losses of the graphite. The capacity of the cell is, hence, limited by the capacity of the graphite electrode. A stable behaviour can be found for more than 30 cycles. There is a small fading of the capacity over the time of the experiment but the feasibility of a graphite/LiCoO₂ type reversible battery is shown, using an ionic liquid based electrolyte, with the only “classical” compound being 5% of the film forming additive VC.

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Notes and references

† The EMI-TFSI used was prepared according to reference 4. It was dried under vacuum at 120 °C for 8 h prior to use and contained less than 20 ppm water. Its electrochemical window was determined by slow scan cyclic voltammetry as –2.1 V and +2.5 V vs. an Ag/Ag⁺ pseudo reference (+1 V and +5.6 V vs. Li/Li⁺) on aluminium and copper metal, respectively. The electrodes were prepared by the doctor blade method on copper (for graphite and the Li₄Ti₅O₁₂) or aluminium foil (for the LiCoO₂). The compositions of the electrodes were as follows: 90 wt% of graphite SFG44 and 10 wt% of Kynar[®] PVdF 1015 (Solvay) in the case of the graphite electrodes, and 85.7 wt% active mass (with Oppanol B200[®] as binder and Ensaco[®] 250 carbon black and TIMREX[®] MB15 graphite as conductive additives) in the case of the Li₄Ti₅O₁₂ and the LiCoO₂ electrodes. The separator was made from an electrochemically neutral glass fibre sheet and the amount of ionic liquid electrolyte used was about 0.35 ml. The electrochemical cycling experiments were conducted in two-electrode titanium-based cells. Cycling of the graphite material was done with 10 mA g⁻¹ during the first cycle and 50 mA g⁻¹ during the subsequent cycles. The potential limits were set to –1.55 V for the reduction and 0 V for the oxidation. These values correspond to approximately 0 V and +1.55 V vs. Li/Li⁺, as the lithium–titanium–spinel shows a large plateau at approximately +1.56 V vs. Li/Li⁺. At the end a potentiostatic step followed until the current dropped below 5 mA g⁻¹. The cycling conditions for LiCoO₂ cells were 30 mA g⁻¹ for delithiation until 2.7 V and lithiation until 1.5 V, followed by a potentiostatic step. These potential values correspond to approximately 4.25 V and 3.05 V vs. Li/Li⁺. VC and acrylonitrile were used as received, the ethylene sulfite was distilled at 5 mbar prior to use. Scanning electron microscopy was performed on a LEO 1530 Gemini microscope. It was operated at low voltage (usually 1 kV) to achieve a suitable contrast of the surface details in the secondary electron images and to minimise charging of the uncoated samples.

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