

Short communication

Aluminium corrosion in room temperature molten salt

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Abstract

Aluminium corrosion in a room temperature molten salt is studied to validate the use of a new kind of electrolyte in a lithium battery. Two solvents have been compared, the room temperature molten salt ethyl-methyl-imidazolium bis(trifluoromethane-sulfonyl)imide (EMI-TFSI), and the liquid organic solvent EC/DMC containing the lithium salt LiTFSI. After confirmation of high aluminium corrosion in the liquid solvent, the results does not show the occurrence of corrosion in the room temperature molten salt.

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1. Introduction

Higher energy and power densities are required from batteries in an ever more demanding world. For lithium systems, taking this under consideration, means high voltage cathodic materials. Therefore, one must find electrolytes, solvents and lithium salts, which remain stable at potentials higher than 4 V versus $\text{Li}^+/\text{Li}^\circ$. It is known that fluoro lithium salts, such as LiPF_6 , and $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ (LiTFSI), stable over a wide potential range are good candidates; especially those in the imides family which are totally stable toward hydrolysis. An interesting family of electrolytes, chemically and thermally stable, showing very good stability at high potentials is based on room temperature molten salts (RTMS) [1–3]. At high potentials, an aspect which also needs to be addressed is the corrosion phenomena. Aluminium is commonly used as a current collector in lithium batteries. The native passive Al_2O_3 layer existing on the metal surface provides protection. Depending on the nature on the electrolyte anions, this passive layer can be broken and then dissolution of the metal occurs. A wealth of results has been published on the corrosive behaviour of lithium salts on aluminium [4–7]. They show aluminium corrosion with LiTFSI in organic solvents [8–12] and a protective effect with LiPF_6 or LiBF_4 [13–15]. In this case, the metal protection is the result of salt degradation forming AlF_3 and/or LiF on the metal surface [16,17].

In the present study, we describe the behaviour of aluminium when using a room temperature molten salt medium. Aluminium corrosion was studied in the room temperature molten salt ethyl-methyl-imidazolium bis(trifluoromethane-sulfonyl)imide, termed EMI-TFSI, for the first time to our knowledge. The results are compared to a liquid organic solvent containing LiTFSI.

2. Experimental

The room temperature molten salt ethyl-methyl-imidazolium bis(trifluoromethanesulfonyl)imide, termed EMI-TFSI, has been prepared in our laboratory from usual synthesis [3]. Its purity was checked by NMR (^1H , ^{13}C , ^{19}F) and cyclic voltammetry. Water content was detected using a Karl Fisher titration and was always less than 50 ppm. The samples were kept in a glove box.

Other products were used as received (LiTFSI 3 M; EC/DMC 1:1, v/v; Tomiyama, Japan). Cyclic voltammetry was performed using a VMP potentiostat-galvanostat from Biologic (Claix, France). The scan rate used was 50 mV s^{-1} .

The electrochemical cell is designed to use small quantities, between 1 and 2 ml. The reference and the counter electrodes were made of silver wires. The reference potential has been measured by adding the highly reversible redox couple butyl-ferrocene/ferricinium to the medium. Its potential was found around +3.2 V versus $\text{Li}^+/\text{Li}^\circ$. The working electrode was Pt, Ni or pure Al (99.99%, Aldrich). Pt and Ni were used to determine the stability potential range of the electrolytes. For measurements near the lithium reduction

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potential ($-0.2\text{ V} \Leftrightarrow +2\text{ V}$), the use of a nickel electrode was preferred to avoid lithium alloy formation.

Platinum and nickel electrodes had a diameter of 100 and 50 μm , respectively. They were polished with alumina powder with particle sizes from 0.3 to 0.05 μm . The electrode was rinsed and immersed in an ultrasonic bath to remove alumina particles, then dried at 80 °C.

Aluminium electrodes were prepared by covering a 0.58-mm diameter aluminium wire with epoxy resin. Then it was very easy in the glove box to cut the extremity of the electrode with a razor blade before each measurement to obtain a fresh aluminium surface without oxide.

3. Results and discussion

3.1. Cyclic voltammetry on platinum and nickel electrodes

The electrochemical window has been determined by cyclic voltammetry on a platinum (or nickel) electrode for the two electrolytes, EMI-TFSI and EC/DMC containing 1 m LiTFSI, using silver wire as a counter and reference electrode. The voltammograms obtained at a scan rate of 50 mV s^{-1} are presented in Fig. 1. The reduction occurred at a less negative potentials for the molten salt than for the EC/DMC solution. The former is reduced around 1.5 V versus $\text{Li}^+/\text{Li}^\ominus$ (-1.7 V versus Ag^\ominus), the reduction of the later corresponds to lithium plating. The oxidation of the EMI-TFSI occurs at a similar potential to the liquid solvent, around 5.6 V versus $\text{Li}^+/\text{Li}^\ominus$ (2.4 V versus Ag^\ominus).

3.2. Cyclic voltammetry on aluminium electrodes

To begin with, the measurement of the initial potential of freshly cut aluminium in the two medium is different.

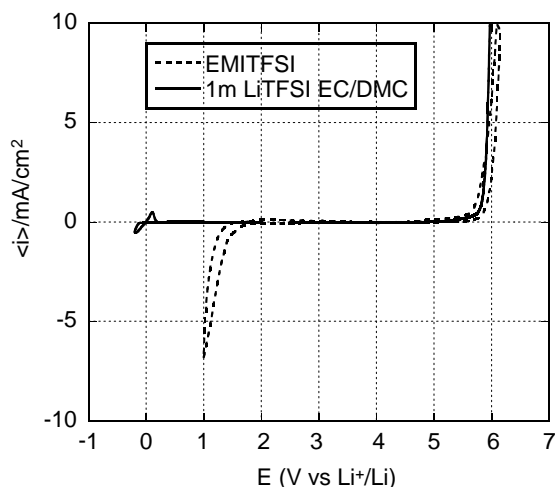


Fig. 1. Cyclic voltammograms obtained on a platinum working electrode ($\varnothing = 100\ \mu\text{m}$) or on a nickel working electrode ($\varnothing = 50\ \mu\text{m}$) measured in EMI-TFSI and in EC/DMC containing 1 m LiTFSI with a scan rate of 50 mV s^{-1} .

In fact, the aluminium electrode is found to exhibit an initial potential of -1.15 V and -1.57 V versus Ag^\ominus just after being immersed in 1 m LiTFSI EMI-TFSI and 1 m LiTFSI EC/DMC solutions, respectively. The standard potential of aluminium oxidation is -1.63 V versus NHE translated as -1.83 V versus Ag^\ominus , our reference. The aluminium open circuit potential (OCP) being more anodic than the standard potential might indicate the existence of a passive layer even after having freshly cut the electrode. The OCP is more anodic in the molten salt medium showing that this medium is less corrosive or more protective than the organic solvent. It will be shown below that this passive layer, probably very thin, is not sufficient to prevent aluminium dissolution.

In Figs. 2 and 3 are compared the behaviour of a freshly cut aluminium electrode in the liquid organic solvent, EC/DMC, to the molten salt solvent with LiTFSI as lithium salt using cyclic voltammetry from the OCP to 2 V versus Ag^\ominus . The anodic limit has been fixed at 2 V versus Ag^\ominus to ensure that no electrolyte degradation occurs in the potential range explored, as is apparent from Fig. 1. As already known [18,19], corrosion occurs in liquid solvent containing LiTFSI and is confirmed by the voltammogram trace in Fig. 2. The first anodic scan, shows a constant current, corresponding to the oxidation of the freshly cut aluminium, devoid of the usual passive oxide layer. Then, the current rises rapidly as the potential reaches 0.5 V versus Ag^\ominus . Considerable increase in current can be attributed to an increase of Al pitting, after the pitting process has been initiated; the pits become increasingly larger. This explains why the corrosion current is still very high, even during the following cathodic scan. Finally, the corrosion current drops to 0

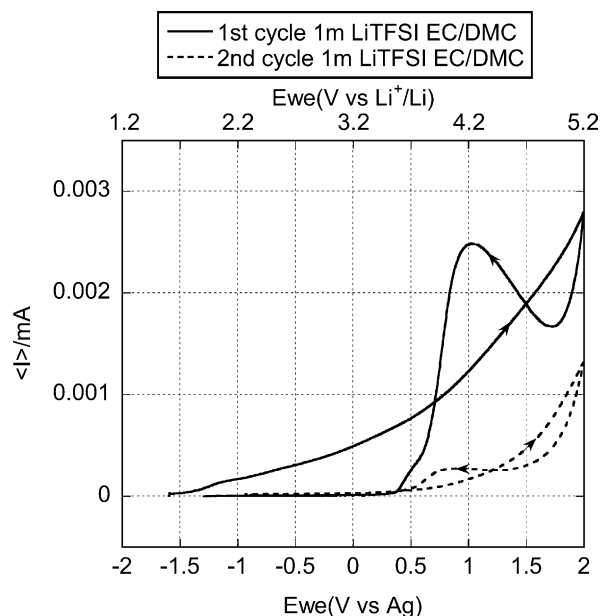


Fig. 2. Cyclic voltammograms obtained on a freshly cut aluminium working electrode ($\varnothing = 0.58\text{ mm}$) in 1 m LiTFSI EC/DMC with a scan rate of 50 mV s^{-1} . The reference is a silver wire.

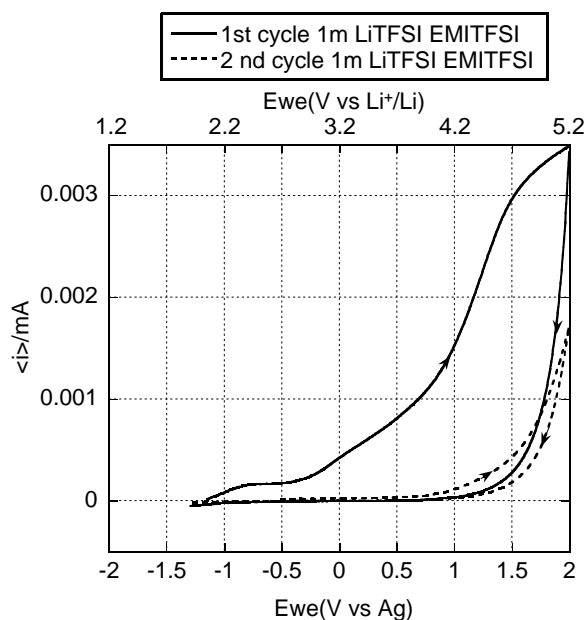


Fig. 3. Cyclic voltammograms obtained on a freshly cut aluminium working electrode ($\varnothing = 0.58$ mm) in 1 m LiTFSI EMI-TFSI with a scan rate of 50 mV s^{-1} . The reference is a silver wire.

at the potential 0.5 V versus Ag° , where the passive layer (Al_2O_3) is formed at the electrode surface.

In the molten salt medium (Fig. 3), during the anodic scan, the behaviour of the aluminium electrode is similar to that observed in EC/DMC. However, at potentials higher than 1.5 V versus Ag° pitting seems to be reduced as the increase is much less dramatic. This is in contrast with the observation for EC/DMC, where the variation in current is quasi-exponential with the voltage. The cathodic scan exhibits a totally different pattern for the two solvents. In fact, the current immediately drops abruptly to 0, indicating that the electrode is passivated. The deposition on the aluminium surface of an insoluble product, probably resulting from the combination of Al^{3+} and TFSI^- , may have occurred. Then, the molten salt EMI-TFSI is able to passivate the aluminium surface and acts as a protection.

The second scan (dashed line) confirms the protective property of LiTFSI in molten salt compared to the liquid solvent. Even after the repassivation of the aluminium electrode during the first cathodic scan, a corrosion current still exists in EC/DMC which is not the case in the molten salt.

4. Conclusion

Cyclic voltammetry on aluminium in the room temperature molten salt EMI-TFSI and in the liquid organic solvent EC/DMC both containing 1 m LiTFSI has been performed. Aluminium corrosion occurring with LiTFSI in organic solvent does not exist in EMI-TFSI molten salt. This result has an important impact in the domain of lithium battery. The possibility to use the lithium salt LiTFSI with its interesting performance and safety properties, in conjunction with aluminium current collectors, is of considerable practical importance. Further experiments to characterise corrosion products are in progress.

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