Short communication

New insight in the electrochemical behaviour of stainless steel electrode in water-in-salt electrolyte

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HIGHLIGHTS

- Cycling potential direction influence the electrochemical behaviour.
- Formation of a film derived from LiTFSI.
- No clear evidence for electrochemically induced formation of LiF.

GRAPHICAL ABSTRACT
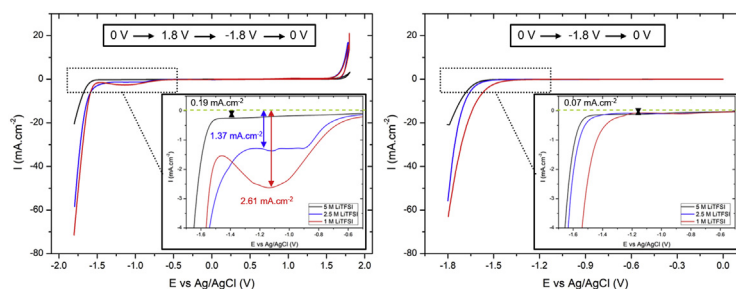
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ABSTRACT

Aqueous electrolytes containing a very high concentration of salt are useful for improving the performance of aqueous rechargeable batteries. These electrolytes, which contain a higher mole concentration of salt than that of water, have only a small amount of free water. Consequently, the electrochemical stability window of various electrodes in such electrolytes is wider than the predicted thermodynamic value of 1.23 V. Moreover, the formation of a solid electrolyte interphase on the negative electrode surface also contributes to the larger electrochemical stability window. In this work, we found that a redox wave corresponding to the electrochemical reduction of bis(trifluoromethylsulfonyl)imide anions in a highly concentrated (21 molal) solution of lithium bis(trifluoromethylsulfonyl)imide is barely observed when the potential range that the electrode is cycled is limited to between 0 and - 1.8 V.

1. Introduction

Water-in-salt electrolytes or superconcentrated electrolytes are currently attracting significant interest because energy storage systems using these aqueous electrolytes should be safer than those using organic electrolytes [1–3]. Water-in-salt electrolytes, which include as a typical example, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) with a high concentration of 21 molal (21 mol of salt per kg of water),

are used in aqueous rechargeable batteries [1,2,4,5] and electrochemical capacitors [6,7]. Other types of superconcentrated aqueous electrolytes include water-in-bisalt [8] and hydrate melt [4]. These electrolytes increase the voltage of energy storage systems well beyond the thermodynamic limit of 1.23 V for water [1,9,10]. This is because the hydrogen and oxygen evolution reactions shift to more negative and positive potentials, respectively [1,11,12]. The wider electrochemical potential stability window is due to the lower amount of free water that

is present in the electrolyte. For a concentration of 21 m LiTFSI, the fraction of free water is only 15%. It has been also proposed that the primary solvation sheath of Li$^+$ is mixed, with on average of approximately 2 molecules of water and 2 TFSI anions, and heterogeneous with Li$^+$(H$_2$O)$_4$ and Li$^+$(TFSI$^-$)$_x$ domains [1,13]. In addition, these two factors influence the chemical composition of the electrode/electrolyte interface, which may contain less water at the electrode surface, and thus may inhibit the hydrogen and oxygen evolution reactions [11]. It is also believed that the formation of a solid electrolyte interphase by reductive decomposition of TFSI anions to mainly form a LiF film enabled an increased battery cell voltage to higher than 3 V. The insulating LiF layer at the electrode surface prevents the contact of water with the electrode surface while allowing lithium-ion transport [1]. Furthermore, it has been recently shown that the solid electrolyte interphase also contains Li$_2$CO$_3$ that would be formed by competitive processes involving the electrochemical reduction of oxygen and carbon dioxide dissolved in the electrolyte [14].

Herein, we provide new insight in the electrochemical processes that occur at the electrode surface with potential cycling in water-in-salt electrolytes. More specifically, the electrochemical behaviour of stainless steel, which is used as a current collector in energy storage systems, is investigated. The influence of the direction of the potential cycling was investigated in order to probe if electrochemical processes are occurring in the potential range of stability of stainless steel (eg. between the hydrogen and oxygen evolution reactions) in the presence of TFSI anions in the electrolyte, and if a solid electrolyte interface is formed. Following potential cycling, the electrodes were characterized by X-ray photoelectron spectroscopy to determine the chemical composition of the films on the electrode surface.

2. Materials and methods

2.1. Solutions

Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was obtained from Solvionic SA. The salt was kept under vacuum at 60 °C before weighing in air. Electrolyte solutions with LiTFSI concentration of 1, 5 and 21 m (mole per kg of water) were prepared with Milli-Q water and kept under nitrogen flow for 2 h before experiments that were conducted at 21 ± 1 °C. These concentrations allow us to compare three different electrolytes: a diluted solution (1 m), a solution in which salt and water amount are similar in mass and volume (5 m), and a super-concentrated solution (21 m) where LiTFSI salt outnumbers water in mass and volume.

2.2. Electrodes and electrochemical cell

The working electrode was a 316 stainless steel (Fe 67.5%/Cr 17%/Ni 13%/Mo 2.5%) foil from Alfa Aesar. The stainless steel electrode was ultrasonically cleaned in high-purity ethanol and Nanopure water, then dried before each experiment. Platinum gauze and Ag/AgCl electrodes were used as counter and reference electrode, respectively. The platinum electrode was ultrasonically cleaned with water and ethanol, annealed in a flame, cooled and washed again in Nanopure water. Electrochemical measurements were performed at 21 ± 1 °C in a two-compartment Pyrex cell with the working and counter electrodes placed in two different compartments that were connected by a glass frit. A Solartron multipotentiostat (model 187) controlled by a computer with the Corrware software was used. Cyclic voltammetry was carried out at scan rate of 10 mV s^{-1}. The cyclic voltammograms shown below is for the first cycle. In one set of experiments, the stainless steel electrode was scanned from the open circuit potential to a negative potential, and in a second set, the electrode was scanned in the positive potential direction. For the latter case, the potential scan was either stopped at 1.8 V or scanned in the negative potential direction, after scan reversal at 1.8 V. Between these different cycling procedures, the electrode was

cleaned with the method described above.

2.3. Physical characterization

X-ray photoelectron spectra were recorded using a VG Escalab 3 MKII spectrometer employing a focused, achromatic Mg K$_\alpha$ source (hν = 1253.3 eV), with the X-ray gun set to 300 W and X-ray incident angle of 90°. All spectra were recorded on a 2 × 3 mm surface with a pass energy of 100 eV for survey scans and 20 eV for high-resolution scans. After cycling in an appropriate potential range, the electrodes were ultrasonically cleaned with Nanopure water, rinsed two times with water and dried under vacuum at 60 °C overnight. The samples were pre-pumped in a preparative chamber to a pressure lower than 6.7 × 10^{-9} mbar before transfer into the analytical spectrometer chamber for measurement. The high-resolution spectra were corrected to the C1s peak at 284.5 eV. The atomic concentrations (at. %) of each element were determined from the relative peak areas of the survey spectra and the corresponding sensitivity factors (C1s = 0.25; O1s = 0.66; Cr2p = 2.30; F1s = 1.00; Fe2p = 3.00) and the equation:

$$\text{at. \%} = a. \ \% = \left(\frac{A_i / s_i}{\Sigma \left(\frac{A_i}{s_i} \right)} \right)$$

where A$_i$ is the area of the peak for element 1 and s$_i$ is the sensitivity factor of the element.

3. Results and discussion

The electrochemical behaviour of a stainless steel 316 electrode was investigated by cyclic voltammetry in different concentrations (1, 5 and 21 m) of aqueous LiTFSI solutions. Fig. 1 (red curves) shows the first set of voltammograms recorded by initially cycling in the positive potential direction. The electrochemical activity for the hydrogen and oxygen evolution reactions decreases with increased LiTFSI concentration. A significant shift of the curves corresponding to the hydrogen and oxygen evolution reactions is observed in the more concentrated LiTFSI (21 m) solution compared to the less concentrated solutions. This is clearly demonstrated when the cyclic voltammograms in the three solutions are superimposed (see Graphical Abstract). The observed shift is due to the smaller amount of free water in the more concentrated solution [1,5]. A well-defined oxidation wave is noticeable at about 1 V on the cyclic voltammograms in Fig. 1 D, E and F. The current intensity of this wave decreases when the LiTFSI concentration increases from 1 to 21 m. The nature of the redox processes giving rise to this oxidation wave is unclear, but it could be associated with the electrochemical oxidation of stainless steel. In this case, the smaller current in the 21 m solution suggests the stainless steel is more resistant to corrosion, as previously observed for aluminum in the same solutions [5]. On the return scan, the relatively weak reduction wave at about 0 V is related to the aforementioned oxidation wave. A reduction wave is clearly observed (Fig. 1 D, E and F) before the onset of the hydrogen evolution reaction. The current intensity of this wave becomes smaller with an increase of the LiTFSI concentration. These observations are in excellent agreement with those of a recent report that were explained by the presence of a passivation layer formed by electrochemical reduction of TFSI [1]. This passivation layer is believed to shift the onset of the hydrogen evolution reaction to a slightly more negative potential. The fact that the current is smaller for the more concentrated solution is intriguing and deserves some comments. Indeed, if the electrochemical reduction of TFSI anions was involved, then one might anticipate that the current becomes larger when the LiTFSI concentration is increased. The experimental observation shows the opposite trend, which is tentatively explained by the formation of a passivation film that is more favourable in a high concentration of LiTFSI salt because more salt is available to form this layer. On the other hand, it should be noted that