Anodic dissolution suppression of the aluminum current collector in high voltage stable electrolytes containing lithium imide salts

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Almost all commercial lithium ion batteries are based on $LiPF_6$ as state-of-the-art electrolyte salt [1]. The choice of $LiPF_6$ is related to its overall well-balanced properties, however not on the basis of any single outstanding property [2]. Besides good conductivity, electrolytes containing $LiPF_6$, show good electrochemical stability (4.8 V vs. Li/Li$^+$ in sulfolane [3]) and suppress the anodic dissolution of the aluminum positive electrode current collector [4].

However, commercial electrolytes typically contain traces of water as an impurity, which promote the decomposition of the $LiPF_6$ salt at elevated temperatures (> 40 °C) as well as high potentials (> 4 V vs. Li/Li$^+$) [5]. Lux et al. investigated the thermal degradation of $LiPF_6$ using spectroscopic ellipsometry to monitor the formation of HF at 50 °C by following the etching rate of a SiO_2 layer on a silicon wafer. Furthermore, they proposed a catalytic pathway for the reaction of HF with SiO_2 in battery electrolytes [6]. As a decomposition byproduct HF is formed, which reacts with the materials of the positive electrode, yielding in the formation of water. Hence, the decomposition of $LiPF_6$ continues until all water molecules are consumed, representing one reason for the cell performance degradation [5].

For future applications, such as electric vehicles, improvements with regard to the energy and power density are required. Thus, an increase of the capacity of electrode materials or the cell voltage is needed. With the development of high voltage materials such as spinels (e.g. $LiNi_{0.5}Mn_{1.5}O_4$ [7]), the need for electrolytes with a high stability against oxidation grows.

Recently, Placke et al. reported so-called "dual-ion cells". In this system, during charging lithium ions are intercalated/deposited into/on the negative electrode material and at the same time anions are intercalated into a graphitic positive electrode. The reversal processes take place during discharge. Depending on the upper cut-off potential and cycling temperature, coulombic efficiencies of more than 99% were obtained. Since the cell potential achieves 5 V vs. Li/Li$^+$ or even more, high voltage stable electrolytes are demanded [8, 9].

In Figure 1 the anodic stability of 1 M LiTFSI in EMS is depicted, demonstrating oxidative electrolyte stability up to around 5.7 V vs. Li/Li$^+$ (assuming 0.1 mA cm^{-2} as criteria). In comparison, organic carbonate solvents exhibit anodic stability up to 4.7 V [10].

Alternative salts are required with an improved thermal and chemical stability. A promising class of alternative salts is lithium imide salts [1].

One example of this class of salts is lithium bis(trifluoromethylsulfonyl) imide (LiTFSI), which was first introduced by Armand [11] and has been intensively studied by many groups. In addition, LiTFSI possesses much greater thermal and hydrolytic stability than $LiPF_6$,

which leads to an enhanced safety of the cell [12].

A major drawback of lithium imide salts is the severe anodic dissolution of the aluminum cathode current collector in organic solvent based electrolytes. In a 0.3 M LiTFSI-PC based electrolyte, anodic dissolution of aluminum already proceeds at around 3.8 V vs. Li/Li$^+$ [13].

In this contribution, high voltage stable solvents, such as sulfones, e. g. ethyl methyl sulfone (EMS), are investigated in combination with lithium imide salts and different electrolyte additives with regard to the anodic dissolution of the aluminum current collector.
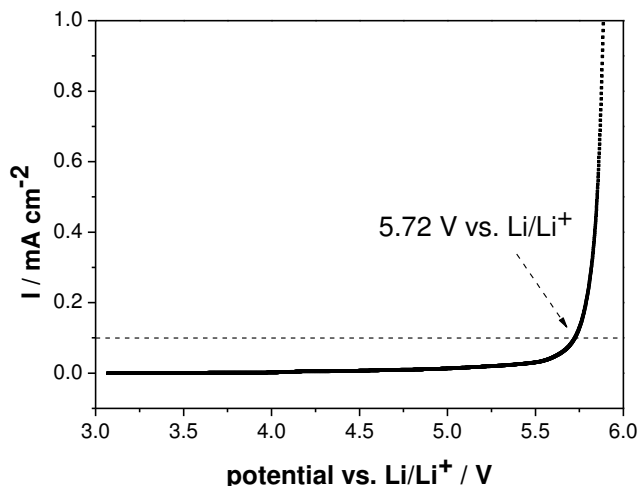

Figure 1: Anodic stability of 1 M LiTFSI in EMS. CE and RE: Li metal, WE: Pt, scan rate 1 mV/s.

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