



# The Effect of 1-Pentylamine as Solid Electrolyte Interphase Precursor on Lithium Metal Anodes



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## ABSTRACT

In this study, the formation of an artificial primary solid electrolyte interphase on a fresh Li surface, via reaction with 1-pentylamine (PA), is reported, allowing removing the influence of the metal electrode's prior history. Electrochemical impedance spectroscopy, galvanostatic cycling, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) are used in order to investigate the effect of PA as solid electrolyte interphase precursor on Li metal. It is shown that pretreating native SEI-free Li metal surfaces with 1 M PA in *n*-pentane sharply decreases the electrode impedance and overpotential with respect to the treatment with only *n*-pentane. The treatment with 1 M PA in *n*-pentane results in surface roughening, but no increase of dendrite formation upon cycling. However, the use of higher PA concentration (5 M) increases impedance and overpotential and leads to dendrite growth.

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## 1. Introduction

Metallic lithium is an optimal anode material for next-generation rechargeable batteries due to its high theoretical specific capacity (3860 mA h g<sup>-1</sup>) and low negative electrochemical potential (-3.040 V vs. standard hydrogen electrode). However, Li dendrite and mossy lithium formation often occur during electrochemical cycling, resulting in safety hazards, short cycle life and low coulombic efficiency and thus preventing the broad commercialization of Li metal batteries, so far [1]. On electrodes such as lithium metal anodes a passivation layer is formed known as solid electrolyte interphase (SEI). The first SEI (called native SEI) is directly generated when Li gets in contact with atmospheric gases, such as CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub>, during its production. We recently investigated the properties of the native SEI using DFT simulations and showed the increase in stiffness and decrease in the work function, *i.e.*, increased ability to reduce electrolyte when Li metal is covered with a small adlayer of *e.g.* lithium oxide [2]. The secondary SEI forms when the lithium is assembled into a cell. In fact, the electrolyte gets decomposed due to the low negative electrochemical potential of Li, thus changing the composition and thickness of the SEI.

An ideal SEI should suppress the further reaction of the electrolyte as well as dendrite growth, on the lithium surface by conducting only Li<sup>+</sup> ions while preventing electrons to reach the electrolyte interface, *i.e.*, it should act as electronic insulator. Ideally, it has a uniform morphology and composition to ensure the homogeneous current distribution, otherwise it frequently leads to mechanical stress and dendrite formation [3]. It should be elastic and flexible to stand shape and volume changes upon the underneath occurring plating and stripping of the electrode while suppressing the penetration by Li dendrites [4–6]. In practice, however, SEIs formed with several liquid and even solid electrolytes tend to break during repeated electrochemical cycling. In the cracks, fresh Li is exposed to the electrolyte, which leads to formation of fresh SEI by decomposition of the electrolyte as well as promotion of dendrite formation. Different approaches have been explored, such as addition of additives or ex-situ formation of artificial layer, to ensure the formation of high quality SEIs [7,8]. In the late 1980s, Aurbach *et al.* prepared fresh Li surfaces by scraping of Li foils or cutting Li rods with wires and studied the reactions of Li with alkyl carbonate solutions [9–11]. In the 90s, Wang *et al.* and Zhuang *et al.* used vapor deposition to produce clean Li surfaces in ultrahigh vacuum (UHV) and investigated the reaction with oxygen, tetrahydrofuran, propylene carbonate, carbon dioxide and water [12–15]. Nevertheless, there are hardly any studies including electrochemical characterization except by Aurbach *et al.* [16,17].

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In this study, we report the effect of 1-pentylamine as SEI precursor for Li metal anodes. To the best of our knowledge, it is the first publication showing combined results of electrochemical impedance spectroscopy (EIS), galvanostatic cycling, scanning electrode microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) to characterize the SEI directly formed on Li metal without any native SEI. For this purpose, a device was developed to cut thin Li slices immersed in the artificial primary SEI precursor solution. These pretreated Li electrodes were assembled in symmetric cells for the further investigation. To characterize the surface morphology of the Li metal electrodes after the SEI formation and further cycling, an automatically opening transport case was in-house designed and realized to transfer the samples under Ar atmosphere into the SEM antechamber.

## 2. Experimental

### 2.1. Materials

Lithium rods (99.9% trace metal basis, 12.7 mm diameter) and anhydrous pentane (>99%) were purchased from Sigma-Aldrich while dimethyl carbonate (DMC, battery grade) was purchased from Powerlyte. 1-pentylamine ( $\geq 98\%$ , Merck) was dried for at least 48 h using molecular sieve with a pore size of 4 Å. N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>14</sub>TFSI) was synthesized via an established procedure [18] and dried at 120 °C for 18 h using a turbomolecular pump (vacuum  $< 10^{-7}$  mbar). This process ensured the water content below 2 ppm, as verified by coulometric Karl Fischer titration (C30, Mettler Toledo). Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99.9%, battery grade, 3M) was dried at 120 °C under vacuum for 36 h. LiTFSI and Pyr<sub>14</sub>TFSI were mixed in the 2:8 molar ratio. Tungsten wire from Alfa Aesar (99.95%, 0.2 mm diameter) was used to slice the Li electrodes. All materials were stored in a glovebox (O<sub>2</sub> content <0.1 ppm, H<sub>2</sub>O content <0.1 ppm, LABmaster Pro DP, MBraun).

### 2.2. Preparation of the electrodes

Lithium electrodes with a freshly generated surface were prepared inside a glovebox as illustrated in Fig. 1. Pieces of 1.5 cm

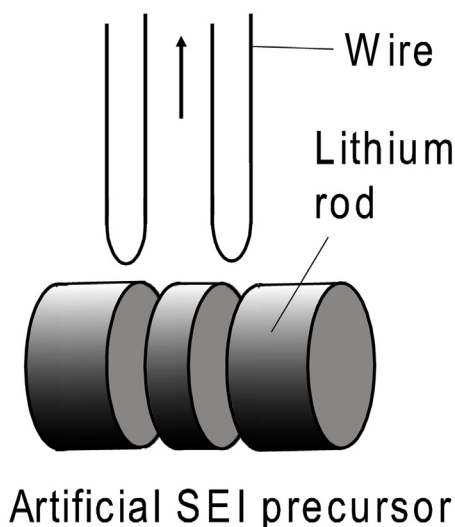


Fig. 1. Scheme of preparing fresh lithium surfaces immersed in artificial SEI precursors.

length were cut from lithium rods using a scalpel. During this procedure, the Li rod was held inside a polypropylene (PP) cylinder in order to preserve the shape of the soft metal. For preparing fresh surfaces in solution, a device was in-house developed and manufactured out of polypropylene (PP), as illustrated in Fig. S1. The lithium metal cylindrical chunk was placed between the two jaws (A, B) inside the beaker (C) while the SEI precursor was added through small channels (D). By turning the winder (E), the tungsten wires cut lithium metal with a smooth surface. The two wires were placed in between three spacers (PP) (F) which ensures a disk with a reproducible thickness (2.3 mm). As tungsten is chemically inert to lithium, it does not contaminate the SEI. The electrodes with flat surfaces have an active area of ca. 1.27 cm<sup>2</sup>.

### 2.3. Cell preparation

All cells were prepared in an Ar-filled glovebox. The symmetric cells were assembled in ECC-PAT-Core cells (EL-CELL) using preassembled insulation sleeves with Li-reference ring and separator (0.26 mm thick glass fiber separator, EL-CELL). The electrodes with a diameter of 12.7 mm were centered using rings made of polypropylene (PP). 120  $\mu$ L LiTFSI-Pyr<sub>14</sub>TFSI were used as electrolyte. Both lithium electrodes, i.e., working and counter electrode, were pretreated to avoid cross-effects.

### 2.4. Electrochemical characterization

All symmetric cells were stored for one week in a KB115 climatic chamber ( $\Delta T = \pm 0.1$  °C, Binder) at 20 °C prior to cycling. Once per day, electrochemical impedance spectroscopy was performed on the cells to monitor their change of interfacial resistance over time. Frequencies from 10 mHz to 200 kHz were applied using a VMP3 (BioLogic).

All cells were cycled galvanostatically at 20 °C (KB115, KB400, Binder) applying a current density of 0.1 mA cm<sup>-2</sup>, which was reversed every 60 min using a battery cycler (S4000, Maccor Inc.). Cut-off potentials of  $\pm 0.5$  V vs. Li reference electrode were used for both working and counter electrode. In order to ensure an equal temperature distribution inside the cell a 30 min rest step was added before each test. After 50 and 100 galvanostatic cycles, the cells were left 30 minutes in rest to ensure electrolyte concentration gradient and temperature equilibration, prior to record electrochemical impedance spectra. All impedance data presented in this publication are referring to only the working electrode. The error bars in the figures represent the standard deviation from the mean value of different cells.

### 2.5. Scanning electron microscopy

The morphology of the electrodes was investigated using high-resolution scanning electron microscopy (LEO 1550VP Field Emission SEM, Zeiss). Each side of the electrodes was rinsed using 1 mL DMC to remove residues of the electrolyte or SEI precursor. Since the samples are sensitive to air, a transfer case was designed in-house and manufactured to transport the electrodes under argon atmosphere from the glovebox into the antechamber of the SEM (Fig. 2). There, the box was evacuated and flushed with gas afterwards. A one-way valve (Blitzventil, Alligator) assures keeping the vacuum inside the box. After removing the knurled nut in air the case stays closed due to the vacuum inside the box. When applying vacuum again the lid opens as soon as the outer pressure gets close to the pressure inside the case due to a spring inside the hinge (Heyman Manufacturing GmbH). The technical drawings are provided in the supporting information.

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