# Non-linearity of the solid-electrolyte-interphase overpotential☆

## Michael Hess*

ETH Zurich, Laboratory of Nanoelectronics, Department of Electrical Engineering and Information Technology, 8092 Zurich, Switzerland

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ABSTRACT

In today's modeling and analysis of electrochemical cycling of Li- and Na-ion batteries, an assumption is often made regarding the interphase that forms between the active material and liquid electrolyte at low potentials, the so-called solid-electrolyte interphase (SEI). The SEI is generally assumed to act like an Ohmic resistor despite its complex chemical composition and porosity distribution. Here, one reports that this assumption does not hold for alkali-ion batteries. The SEI possesses a non-linear overpotential characteristic which saturates already at low current density of 0.1 mA cm$^{-2}$ giving only $3.3 \pm 1$ mV for Li-metal electrodes in different electrolytes. For Na- and K-metal electrodes, these SEI overpotentials become dominating with 31 mV and 72 mV at the same low current densities giving significant disadvantages over Li-ion batteries for commercial applications. With the introduction of a new term, one achieves agreement between the parameters from galvanostatic cycling and electrochemical impedance spectroscopy for the first time. The discovery of the non-linear SEI overpotential disrupts the general believes about the role of the SEI for today's batteries as it is basically negligible for Li-ion batteries at room temperature.

## 1. Introduction

Li-ion batteries are the most-widely used rechargeable battery type when it comes to high energy density applications such as laptops and electronic gadgets. In contrast to NiMH or lead-acid batteries which operate in aqueous electrolytes and are limited to 1.5 V, Li-ion batteries operate in organic aprotic electrolytes allowing them to be cycled to over 4.2 V [1,2]. However, one significant drawback associated with such potential window is the instability of the organic electrolyte leading to surface film formations on the active materials, i.e. the so called solid-electrolyte-interphase (SEI) on the negative electrode [1,3–5].

This SEI has been the focus of intensive research since the beginning of Li-ion batteries in the late 1980's where the different SEI compositions and reduction potentials have been well characterized as a function of the used electrolytes [1,3]. In general, the inner SEI consists of a very dense layer of 2–10 nm of mainly inorganic reduction products with low oxidation states like $Li_2O$, $LiF$ and $Li_2CO_3$, while the outer SEI is relatively porous with various inorganic, organic and polymeric reduction products of higher oxidation states like $ROCO_2Li$, $ROLi$ (R-alkyl), poly-carbonates, $LiOH$, and salt derivatives like $Li(As,P,B)F_y$ with an estimated thickness of circa 10–100 nm [3,5,6].

Fig. 1 shows a sketch of the mechanism that is believed to govern charge and mass transport through the SEI. First, electron transfer reactions occur between the Li-metal surface and the inner dense SEI which can be modeled by the Butler-Volmer equation. Ionic transport occurs within the inner SEI and the ions get solvated at the interface of the inner and porous outer SEI. While Li-ion transport in the porous outer SEI layer can be easily described by electrolyte diffusion with some porosity and tortuosity, the ion transport in the inner inorganic SEI layer is still under debate.

Two main mechanisms are proposed. One the one hand, little micro-porosity might remain where only non-solvated Li-ions penetrate through to avoid electrolyte reduction [3]. On the other hand, ionic conduction could occur along the grain boundaries of the decomposition products in the inner SEI [3]. However, ionic conduction through the "bulk" SEI has been ruled out by electrochemical impedance spectroscopy (EIS) measurements of the dry SEI with blocking counter electrodes by Gaberscek et al. leading to resistances of more than $20'000\,\Omega cm^2$ [7] whereas standard SEI resistances in liquid electrolytes range from 40–$100\,\Omega cm^2$ [5,7–9]. More recent characterizations of the SEI using ferrocene point out that the electron migration through the SEI cannot explain the shuttle mechanism of different additives for

**Fig. 1.** Schematic of SEI and involved processes: sketch of the solid-electrolyte interphase that forms on alkali-metals with an inner inorganic non-porous layer and an outer highly-porous layer of organic, inorganic and polymeric electrolyte reduction products, transport processes are indicated on the right side including surface reactions, ionic transport through the inner SEI, solvation at the inner-outer SEI interface and electrolyte transport through the outer porous SEI.

overcharge protection but solvent penetration into the inner SEI layer could [6]. However, in a follow up, Tang et al. estimate the porosity based on the time constant of a ferrocene step function which, according to the authors, "yields porosity values on the order of $10^{-15}$" [10]. While the first study of EIS on a dried SEI [7] might be misleading due to the much thicker outer SEI made from badly conducting polymers, the porosity estimates with ferrocene [10] seem to be reasonable as any species in contact with bare Li-metal in the remaining porosity of the SEI would react within milliseconds non-selectively [11] and close the pore with solid reduction products.

Additionally, several electrochemical measurements about the resistivity of the SEI seem to be off. Most measurements concentrate on electrochemical impedance spectroscopy where the first semicircle is usually ascribed to the SEI resistance [3,5,12]. In literature, this semicircle is sometimes "fitted" by up to four [8] or five [5,9] linear RC elements describing different layers of the SEI where the total SEI resistance is $66\,\Omega\text{cm}^2$ [8], between 40–$100\,\Omega\text{cm}^2$ depending on the used salt [9] or even up to $800\,\Omega\text{cm}^2$ for 1 M LiPF$_6$ in propylene carbonate stored for 24 h [5]. These resistances are substantially higher than the electrolyte resistance with $3.6\,\Omega\text{cm}^2$ [8] or surface reaction resistances with 13–$20\,\Omega\text{cm}^2$ for LiPF$_6$ and LiClO$_4$ in different alkyl-carbonates [13]. Thus, the SEI would be the main limiting factor for Li-ion batteries. If the SEI resistance determined from EIS would hold for galvanostatic measurements, the overpotential from the SEI of 40–$800\,\Omega\text{cm}^2$ [5,8,9] at 10 mA cm$^{-2}$ would be 0.4–8 V from one electrode alone.

Here, one shows that the resistance from EIS is correctly determined, however, the SEI resistance is highly nonlinear. First, one performs galvanostatic cycling on symmetrical Li-Li, Na-Na, and K-K batteries with various electrolytes of mainly PF$_6^-$ and ClO$_4^-$ in ethylene carbonate mixtures (EC) or pure propylene carbonate (PC). An additional equation is proposed merging the SEI resistances determined from galvanostatic and EIS experiments. These findings have important implications for all battery configurations where alkali-metal electrodes are used as a counter or reference electrode, the so called half-cell configuration commonly used to measure active materials individually.

## 2. Experimental

Dry Li-foil (Alfa Aeser, 99.9%), dry Na-rods (Acros, 99.8%), and K-cubes in mineral oil (Aldrich, 99.5%) have been cleaned from oxidation layers and used to prepare 13 mm diameter electrodes. These electrodes were prepared in an Argon filled glovebox with continuous removal of O$_2$, H$_2$O and organic volatiles.

Ethylene carbonate EC (Aldrich, anhydrous 99%), propylene carbonate PC (Aldrich, anhydrous 99.7%), dimethyl-carbonate DMC (Acros, extradry 99+%), diethyl-carbonate DEC (Acros, anhydrous 99%) were additionally dried over 4 Å molecular sieves for at least six weeks after which 16 ppm of trace water was still present measured by Karl-Fischer-Titration. Electrolytes for Li were purchased in prepared state being 1 M LiPF$_6$ in either EC:DMC 1:1 wt (LP30), EC:EMC 1:1 wt (LP50), EC:DEC 1:1 wt (LP40), or EC: DEC 1:1 wt with the addition of 2 wt% vinyl-carbonate (all from Novolyte/BASF).

The salts LiPF$_6$ (Strem Chemicals, 99.9+%), LiClO$_4$ (Aldrich, ampoule 99.99%), Li-bis(oxalato)borate LiBOB (Aldrich), Li-bistri-fluoromethanesulfonimidate LiTFSI (Aldrich, 99.95%), NaPF$_6$ (Alfa Aesar, 99+%), NaClO$_4$ (Acros, 99+%), KPF$_6$ (Strem Chemicals, 99.5%), KClO$_4$ (Acros, 99%) were vacuum dried at 25 °C for one day before use. The solvents were prepared in weight equivalent mixtures. The salt was added based on the calculated density of the pure solvent mixture without the salt leading to a systematic error of circa 3-4% lower molarity than 1 M (see Suppl. Note 1).

Whatman glass microfiber filters (GE Healthcare, GF/D 1823-257) were heated inside the glovebox to 400 °C to remove adsorbed water and are mainly used due to their very high porosity of circa 70% after compression to circa 200 $\mu$m at p = 50 Ncm$^{-2}$ in the coin type cells made from titanium. For comparison, also commercial separators Celgard 2325, M824, PP1615, K1640, Targray PP16, PE16A, another commercial separator producer with a PE mono-layer of 20 $\mu$m and Whatman (GE, 0.25 mm, 1820-240) have been used. Galvanostatic cycling (GS) and electrochemical impedance spectroscopy (EIS) were performed with Biologic VMP3 and MPG2 cyclers at room temperature 25 ± 2 °C. More details can be found in Suppl. Note 1.