Electrochimica Acta 269 (2018) 331–339

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Solid electrolyte interphase: Can faster formation at lower potentials yield better performance?

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ARTICLE INFO

Article history:
Received 24 March 2017
Received in revised form
14 February 2018
Accepted 1 March 2018

Keywords:
SEI formation
Li-ion battery
Pre-charge
Composite carbon electrodes
Cyclic voltammetry

ABSTRACT

To make a Lithium Ion Battery (LIB) reliably rechargeable over many cycles, its graphite-based negative electrode requires the solid electrolyte interphase (SEI) as a protection layer. The SEI is formed through chemical and particularly electrochemical side reactions of electrolyte components in the first charging cycle(s) after manufacturing of a LIB. The SEI ideally serves two purposes: (i) act as a sieve permeable to Li ions but not to other electrolyte components and (ii) passivate the electrode against further electrolyte decomposition. Core element of conventional SEI formation is a lengthy, low-current galvanostatic charging step, which due to its time consumption contributes heavily to cell manufacturing costs. Here, we report on some non-conventional SEI formation protocols for composite carbon electrodes, inspired by recent experimental findings at smooth model electrodes. Acknowledging that the SEI forms in two main steps, taking place in a high-potential and a low-potential region, respectively, we demonstrate that less time spent in the high-potential region not only makes the process faster but even yields SEIs with superior kinetic properties. We tentatively explain this via basic rules of thin film growth and the role of grain boundaries for ion transport. We also report on the positive influence of multi-frequency potential modulations applied between high-potential and low-potential formation. Given that any new cell chemistry in principle requires its own tailor-made formation process, technologic success of future LIB cells will benefit from a systematic, well-understood toolbox of formation protocols. This paper is meant as a first step, highlighting potentially low-hanging fruits, but also flagging the demand for further systematic studies on model systems and on commercially manufactured cells.

1. Introduction

The first few cycles of a Li-ion battery are referred to as the formation cycles. During these cycles, and in particular during the very first charging, a complex interplay of (electro-)chemical (side) reactions of electrolyte components creates the Solid Electrolyte Interphase (SEI) covering the surface of the negative electrode (anode). For high power/energy densities as well as a long cell lifetime, the SEI should provide good electronic insulation, fast Li^+ conductivity and be stable under both cycling and calendar aging conditions. Core element of conventional SEI formation is a lengthy, low-current galvanostatic charging step, which is supposed to ensure a uniform SEI structure [1–8]. On the other hand, in order to reduce manufacturing costs, formation cycles should be as simple and short as possible. From an industry perspective, these conflicting requirements make it necessary to appropriately adjust the formation protocols in order to compromise between customer expectations in terms of performance and cost [2,3,9–11]. Given that no new cell chemistry is brought to manufacturing level without fine adjustment of multiple electrolyte additives for optimized SEI formation, the formation protocols, i.e., applied currents and potentials, should deserve similar attention and possibly new approaches based on both fundamental and empirical studies.

Matsuoka et al. [12] examined the SEI formation on highly oriented pyrolytic graphite (HOPG), which served as a starting point for another recent study by our group [13,14]. This study identified a two-step formation mechanism with threshold steps occurring at

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https://doi.org/10.1016/j.electacta.2018.03.007

~700 and ~400 mV vs. Li/Li$^+$. The chemical nature of the SEI compact layer formed at the higher potential step (700 mV) differs significantly from that formed below 400 mV. From potentiostatic experiment current transients we concluded that both SEIs passivate the surface against ongoing SEI formation at the same potential. Hence, the low-potential (carbonate and Li containing) must SEI form through further reduction reaction of the compact high-potential SEI. Electrochemical reactions of solvent molecules only play a minor role in the second step. Under this hypothesis, the chemical and physical properties of the final SEI layer could be affected and therefore controlled by controlling the properties of the high-potential layer.

For this paper, we transferred the insights gained at low surface area carbon electrodes (glassy carbon and highly oriented pyrolytic graphite, HOPG [13,15–19]) to graphite powder based electrodes as used in commercial battery cells. Specifically, we used state-of-the-art composite electrodes in three-electrode half-cells (thus investigated only the graphite half-cell behavior) and commercially established electrolyte. We tested new protocols that make use of the separation of the formation process into a high-potential and a low-potential region, appreciating that those two regions may not be equally “valuable”. A conventional constant-current formation process does not actively manage the time spent in certain potential regions, thus possibly leaving room for improvement. Inspired by a coincidental discovery in previous Electrochemical Impedance Spectroscopy (EIS) experiments at HOPG electrodes, we also tested the influence of superimposed multi-frequency potential modulations on the SEI formation process.

The first part of this paper reports on cyclic voltammetry (CV) results that demonstrate the interplay of the high-potential and the low-potential formation regimes and their overall effect on the subsequently SEI-covered negative electrode. Based on those results, three non-conventional but still commercially applicable formation protocols are tested and benchmarked via their performance in subsequent test cycles. We observe benefits of spending less time in the high-potential regime, which we rationalize based on the principles of electrochemical film growth. Our results do not only confirm the potential technologic relevance of the previously discussed two-step SEI formation mechanism, but provide a springboard for a new formation parameter space to optimize SEI formation. This has the potential to not only speed-up the formation process in commercial cell manufacturing (where it is one of the most costly production steps [20]) but also to improve the performance of the negative electrode altogether.

2. Experimental

2.1. Setup

Investigated electrodes consisted of MAG-D20 graphite (Hitachi Chemical), 2%wt CMC/SBR binder (Dow Chemical/JSR, respectively) and 2%wt Super-C65 carbon (Timcal) as conductive agent. The demineralized water-containing slurry was coated on 10 μm thick copper foil (Schlenk) with a total loading of ~7 mg cm^{-2}. After predrying, calendaring to a porosity of 35% and punching, electrodes were finally dried at 120 °C for 12 h in a vacuum oven (~10^{-2} mbar, Glass Oven B-585 Drying, Büchi Labortechnik). The electrolyte used was EC:EMC 3:7 with 2%wt VC and 1 M $LiPF_6$ (LP572, from BASF). Electrodes were transferred without atmosphere contact into an Argon filled glove box, where they were weighted individually for a first capacity approximation. The other cell components were cleaned with iso-propanol and demineralized water in an ultrasonic bath and then dried at 60 °C before being transferred into the glove box for cell assembly. The glove box contained <0.1 ppm water and <3 ppm oxygen. CV experiments were performed in T-shaped ECC-Ref cells with glass fiber separator with 75 μm thickness (both from EL-Cell) soaked with 250 μl of electrolyte. The potentiostat used for CVs was a Bio-Logic VMP 3. All other experiments were performed in Swagelok type T-cells including a Celgard 2325 PP/PE separator soaked with 80 μl of electrolyte. Cells were cycled using a Maccor Series 4200 cycler. In both EL-Cells and Swagelok type cells, counter and reference electrodes were separated and made of Li foil (Alfa Aesar), thus all experiments were performed in three-electrode half-cell configuration. This ensures that any potential changes reflect changes of the graphite working electrode since they are measured against the current-free reference. Any deteriorations of the Li counter electrode, which may well occur, will demand more polarization of that electrode for any given current, but that would not affect the potential determined for the working electrode.

After cell assembly and sealing, cells rested for ~3 h before applying external currents or voltages in order to avoid poor electrode wetting.

2.2. Test protocols

If not otherwise stated, cells were formed with one of the formation protocols described in the following section. The given rates were calculated based on the electrode active mass loading and a capacity density of 360 mAh g^{-1}. After formation through one of the described protocols, the cells were stored at room temperature for another 5 days. Before being tested, cells were conditioned and the effective capacity was determined. C-rates of testing protocols and state of charge (SOC) calibration are calculated from this effective capacity. All tests were performed in a climate chamber at 25 °C. In the sections below, lithiation and delithiation of the electrode will be referred as charging and discharging, respectively.

2.2.1. Formation protocols

While the formation protocols of commercial cell production lines are kept under lock and key by the manufacturers, we have chosen a “standard formation protocol”, broadly used in laboratories and research production lines, as our benchmark [4–8]. Against that benchmark, we tested three non-conventional formation protocols (see details of all four protocols below). The latter are either inspired by our previous work [13,14] mentioned above or by CV experiments presented below. The specific fundaments are elucidated in the respective discussion sections. Briefly, combinations of sequential high- and low-rate galvanostatic and of potentiostatic steps allow us to control the time spent in different potential regions. Furthermore, we demonstrate the effect of small potentiostatic oscillations as part of the SEI formation protocol. Unless otherwise stated, from here on all potentials are given vs. Li/Li$^+$.

Fig. 1 depicts the standard benchmark and the three non-conventional formation protocols used in this study. The current rate ordinate units are shown as fractional C-rates. The dashed FC-arrows indicate that, after the profile shown in Fig. 1, further cycling (FC) is performed.

2.2.1.1. Standard formation protocol (benchmark). <i> charge at 0.1 C until potential $\leq$ 20 mV; <ii> maintain 20 mV until current $\leq$ 0.05 C; <iii> discharge at 0.1 C until potential $\geq$ 1.5 V. <iv> charge at 0.1C to 50% SOC (based on calculated/predicted capacity). Charging and discharging phases were separated by 20 min relaxation phases. Fig. 1 depicts only the first charging half-cycle (steps <i> and <ii>, respectively), while the FC-arrow represents the subsequent phases.

2.2.1.2. High-rate formation protocol. Similar to the standard