Nano Energy (2013) 2, 713–719

Available online at www.sciencedirect.com

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RAPID COMMUNICATION

Determination of mechanical properties of the SEI in sodium ion batteries via colloidal probe microscopy

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Received 1 July 2013; received in revised form 21 August 2013; accepted 26 August 2013
Available online 31 August 2013

KEYWORDS
Solid electrolyte interphase;
Sodium ion battery;
Force spectroscopy;
Colloidal probe microscopy

Abstract
The solid electrolyte interphase (SEI) is a layer that forms at the anode surface for all alkali metal ion batteries which utilize liquid electrolytes. It acts as an electronic insulator and ion conductor, but the formation of the SEI results in an irreversible capacity loss. For high capacity anodes in sodium ion batteries (NIBs), continued cycling of the battery ruptures the SEI and exposes new areas of the anode surface where the electrolyte will reduce. In this work, we utilize colloidal probe microscopy to investigate the mechanical properties of the SEI layer in NIBs for use in future anode designs. Our results indicate a lateral inhomogeneity in the Young's Modulus on the micron scale spanning 3 orders of magnitude. This technique can be used to investigate the differences in the SEI formed by different electrolytes and electrolyte additives and ultimately to determine the best liquid electrolyte for NIBs.

Introduction

The growing field of renewable energy has necessitated the exploration of efficient and large scale energy storage technologies. Solar and wind energy do not provide a constant source of energy; requiring the integration of energy storage technologies into the grid. At the forefront of energy storage applications are lithium and sodium ion batteries (LIB/NIBs), which provide inexpensive and long lasting energy storage [1,2]. However, the relative expense and safety issues of LIBs make NIBs the more attractive choice for these large scale energy storage demands [2]. Currently, the lifetimes of NIBs are limited due to the degradation of electrode materials and electrolyte upon battery cycling [2,3]. Several groups have reported potential anode systems for NIBs; focusing on carbon based intercalation anodes or high capacity Sn based alloying anodes [2,4–7]. The high capacity alloying anodes experience volume changes up to 400% upon sodiation, leading to failure

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http://dx.doi.org/10.1016/j.nanoen.2013.08.005

by anode pulverization [2,8-10]. More recent studies have mitigated the effects of volume expansion by incorporating engineered Sn composite and nanosized Sn particles [4,7,8]. Ultimately, the extremely high cyclability and capacity retention required for grid scale storage will only be achieved by novel anode design [9].

One way to improve the cyclability of NIBs is to facilitate the formation of a strong and stable solid electrolyte interphase (SEI) [5,11]. The SEI is a passivating layer formed on the electrode surface due to thermodynamic decomposition of the electrolyte [12,13]. Several structures of the SEI have been proposed, including a bilayered structure, multilayered structure, and a mosaic microphase structure [14-16]. The common feature between these structures is that the SEI consists of more reduced compounds at the electrode surface and less reduced components extending into the liquid electrolyte. The composition of the SEI is often characterized with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) [11,12,16]. Organic compounds in the SEI include alkyl carbonates and alkoxides, and inorganic compounds include oxides, alkali carbonates, and various salts [5,14]. SEI formation results in an irreversible capacity loss; this process, therefore, must occur quickly and be self-limiting. The SEI layer serves two beneficial purposes: it prevents further electrolyte and electrode degradation by acting as an electronic insulator, and it strips lithium or sodium ions of the solvation sheath as they insert into the electrode [16,17]. A good SEI should be flexible enough to survive the volumetric changes of the electrode while still maintaining a strong contact with the electrode surface. Hence, characterizing the mechanical properties of the SEI layer is important to develop high performance electrolyte–electrode systems for NIBs.

Several groups have utilized electrochemical atomic force microscopy (EC-AFM) to study the morphology of the SEI for LIBs. Lucas et al. characterized the SEI formation mechanism on Sn anodes, while others characterized the SEI formed on graphitic anodes by various organic electrolytes [18-23]. Zhang et al. combined force spectroscopy with EC-AFM to measure the Young's modulus and layered-structure of the SEI for MnO anodes [24]. The authors found that the modulus of the SEI varies over two orders of magnitude, depending on SEI composition at the measurement location. Additionally they demonstrated that a lower modulus layer can form on top of a higher modulus layer, giving evidence to the bilayered structure prediction. There are inconsistencies in the SEI structure; the majority of their measurements revealed the presence of a single layer SEI.

In this study, we measure the Young's Modulus of the SEI formed in NIBs with colloidal probe AFM. To the best of our knowledge, this is the first study of the SEI in NIBs using AFM. This is also the first study of the SEI layer, both in LIBs and NIBs, utilizing a colloidal tip AFM probe. The force spectroscopy experiments are performed with a colloidal probe to prevent penetration and act as a *de facto* simulation of the forces that anode expansion will impose on the SEI. Several groups have reported that the composition of SEI varies greatly across the anode surface; a large colloidal probe will compensate for this inhomogeneity [5,16,24]. This communication is concerned with measuring the properties of one electrolyte, but the technique can be applied to any organic electrolytes that decompose to form an SEI layer. A quantitative comparison of the mechanical properties of the SEI formed by various electrolytes will provide direct proof as to which electrolyte is best for NIBs.

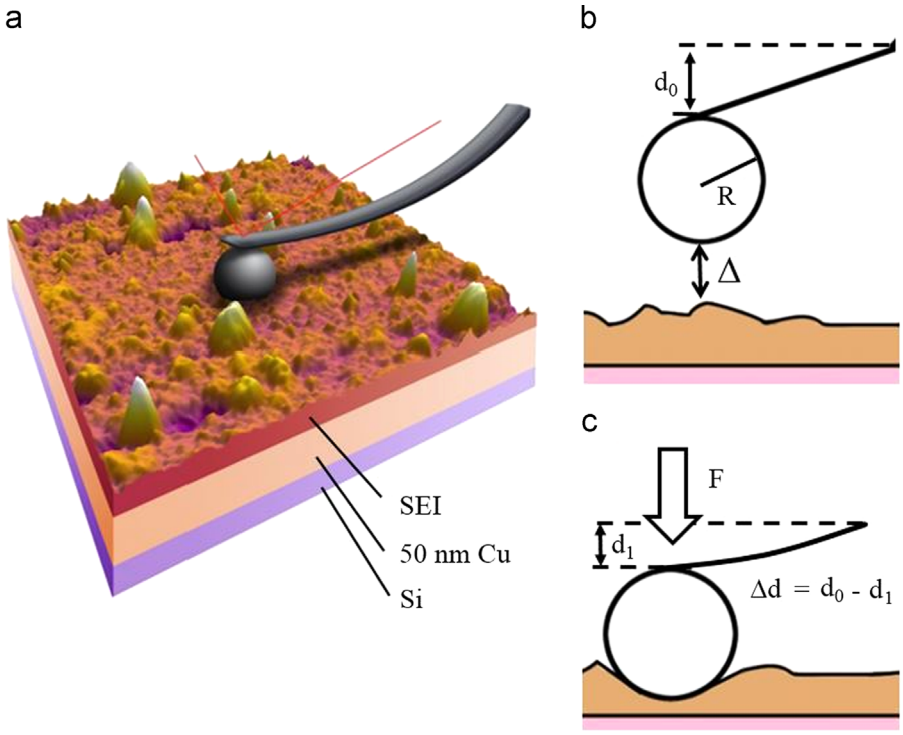

Figure 1 Schematic representation of the SEI layer indented with a colloidal probe. (a) Illustrates the structure of the electrode. The SEI image is 10 μm a side with a height range of 250 nm. During indentation, (b) the probe is lowered towards the surface, and (c) indents the surface after contact.