Rapid Communication

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

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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.

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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

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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](image-url) 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.
Previously, electrolyte performance was indirectly characterized by comparing the cyclability of identical electrode systems in different electrolytes [11]. The results of mechanical property measurements will help to explain why NiB anodes perform better when paired with certain electrolytes.

Materials and methods

The SEI layer is decomposed onto a flat, conductive substrate using cyclic voltammetry (CV). The substrate consists of a 50 nm Cu layer thermally evaporated onto a doped Si wafer (Figure 1(a)). These materials were chosen to provide a flat, stiff, and conductive substrate that will not experience any volume changes during cycling (neither Cu nor Si alloy with Na). The modulus of Cu/Si is reported to be 135 GPa, much larger than the expected range for the SEI [24,25]. The Cu layer thickness is measured with a 6 MHz quartz film thickness monitor (Inficon). Standard half-cells are assembled in an argon glove box with a Cu/Si substrate working electrode, Na metal counter electrode, and 1 M NaPF₆ in 1:1 ethylene carbonate and diethyl carbonate (EC:DEC) electrolyte. This electrolyte has been shown to have good thermal, electronic, and electrochemical properties as well as producing a stable SEI layer. It was found that not washing the samples resulted in the formation of a hard, non-porous layer with a Young’s Modulus over an order of magnitude larger than that of the washed samples. We predict that various salts evaporate out of the electrolyte and form the hard layer on the surface; the acetonitrile prevents this by removing excess electrolyte. Immediately after washing, the morphology of the samples is characterized with AFM and scanning electron microscopy (SEM) to minimize degradation of the SEI layer. SEM characterization is performed with an Asylum MFP-3D AFM (Asylum Research, CA). Tapping mode images of the surface morphology are obtained with a VISTAprobe T300-10 Si probe. Force curves of the samples are obtained in the force spectroscopy mode using an sQube SiO₂ colloidal probe at a tip velocity of 500 nm/s and a trigger point of 0.5 V. The probe diameter measured in ImageJ from a scanning electron micrograph is 6.55 μm, and the spring constant is determined to be 36.8 nN/nm with the thermal K method [27,28]. Deflection sensitivity of the tips is calibrated using a fresh mica surface. Hundreds of force curves in total are collected to measure the Young’s modulus. SEM characterization of the SEI layer is performed with a Hitachi SU-70 Ultra High Resolution Field Emission Scanning Electron Microscope. SEM images of the SEI are compared with the AFM images to confirm surface morphology. The elemental composition of the SEI layer is determined with energy dispersive X-Ray spectroscopy (EDX) using a Bruker silicon drift detector (SDD). A custom MATLAB program, written in the Curve Fitting toolbox, was used to first convert the raw force vs. indentation data in the method described below. A first order polynomial fit is applied to the data, and the slope and R² goodness of fit reported.

Theory and calculations

The colloidal probe force spectroscopy setup is illustrated in Figure 1 (not to scale). Initially the probe is held above the surface of the sample, out of the range of any tip-surface interactions. The probe is then lowered at 500 nm/s towards the surface (Figure 1(b)). The probe contacts the surface and continued driving of the probe exerts a compressive force on the surface. The resulting force profile manifests as an indentation of the surface as well as a deflection of the tip cantilever (Figure 1(c)). A simple Hookean relationship is used to calculate the applied force:

$$F = k \Delta d$$

(1)

where F is the applied force, k the spring constant of the cantilever, and Δd = d₀ - d₁ the deflection of the tip, measured by displacement of a laser spot on a photodiode [29].

The Young’s Modulus of the SEI is extracted from the force profiles using a Hertzian model. The Hertzian model is appropriate in this case as there is minimal adhesion during the approach [30,31]. For paraboloidal indenters, the force-indentation relation is given by

$$F = \frac{4E\sqrt{R}}{3(1-\nu^2)} \delta^{3/2}$$

(2)

where F is the applied load, E the Young’s Modulus, R the tip radius of curvature, δ the indentation depth, and ν the Poisson’s ratio [31]. The indentation depth can be rewritten as δ = C - d₀, where C is a constant and d₀ is the tip-sample separation. Setting C as the contact point allows for the separation to be equal to the negative absolute value of the indentation. By making this substitution, Eq. (2) can be rearranged to fit a linear model of force(2/3) vs. tip-sample separation;

$$F^{2/3} = C^* - \frac{4E\sqrt{R}}{3(1-\nu^2)} \delta * \Delta$$

(3)

where C* is a constant proportional to the tip-sample contact point [31,32]. The Young’s Modulus is therefore extracted from the slope of the linear regime of a force(2/3) vs. separation plot given by Eq. (3) [32]. One assumption of the Hertzian indentation model is that the indented surface is represented as an infinite elastic half space, with no interaction effects due to a substrate with a different modulus. The thickness of the SEI ranges from tens to hundreds of nanometers, and therefore may not be considered infinite for significant indentations [24]. Akhremitchev et al. explored the effects of a hard substrate underneath a thin layer and proposed a correction factor model for the modulus that depends on the layer thickness [31,32]. This model is currently being evaluated for application to our experiments.
Results and discussion

A representative cyclic voltammogram of electrolyte decomposition over 3 cycles is presented in Figure 2(a). The anodic current during the first cycle is much larger than for subsequent cycles, indicating that SEI formation primarily occurs during the first charge cycle. The absence of corresponding cathodic peaks of similar magnitude means that this decomposition is irreversible. Previous studies have shown that EC decomposes around 0.8 V vs. Na/Na$^+$; our CV results confirm this decomposition [17]. The smaller, broader shoulder at 1.3 V vs. Na/Na$^+$ is likely due to the decomposition of the DEC component of the electrolyte; which occurs at a higher voltage than EC [33]. These peaks appear for the second and third cycle as well and are associated with either new SEI formation or further reduction of already decomposed species. For our system the latter is more likely as there is no SEI rupture due to volume expansion of the working electrode [23]. Reduction of copper oxide and other impurities is seen in the first cycle at 2.0 V vs. Na/Na$^+$. At voltages approaching 0 V vs. Na/Na$^+$, Na metal may plate the Cu surface forming Na compounds in the SEI. The small cathodic peaks, therefore, correspond to the removal of Na ions and Na metal deposits. Similar CV behavior is observed for the sample cycled 10 times.

The SEM and AFM images of the SEI surface in Figure 2 (b) and (c), respectively, show that the layer is relatively flat with few particles and pinholes interspersed. EDX analysis (Figure 2(d)) of the layer in SEM reveals a uniform distribution of Na, F, O, P, C elements from both the NaPF$_6$ salt and EC:DEC solvent. Some samples produced a less uniform surface with a larger distribution of surface features; this could be a result of uneven current density across the electrode or an artifact of separator removal within the half cell.

Three hundred and fifty force curves were obtained from various points on each sample using the colloidal probe method described above. The raw data is converted and fit to Eq. (3) using the custom MATLAB program to extract the Young's Modulus of the SEI layer. Figure 3 schematically illustrates the fitted data and relationship between the slope and modulus. An SEM image (Figure 3 inset) of the colloidal probe is used to extract a radius value to input into the equation. The SEI is assumed to exhibit rubber elasticity within the elastic region, therefore the Poisson's ratio $\nu = 0.5$ [24]. Only the linear portion of the indentation region is fitted to Eq. (3); the unfitted portion of the curve in Figure 3 is the ramp up to linear from the initial contact point (due to cantilever deflection) and is therefore not included in the fit. The measured modulus for the 3 cycle samples (207 curves) ranges from 0.57 to 1796 MPa with an average of 304$\pm$7345 MPa, and for the 10 cycle samples (143 curves) the modulus ranges from 3.91 to 756 MPa with an average value of 197$\pm$142 MPa. Over 90% of the fitted curves have $R^2$ values of greater than 0.8. These measured values are consistent with those reported by Zhang et al. [24]. The histograms in Fig. 4(a) and (b) present the distribution of...
moduli for the 3- and 10-cycle samples, respectively. There is a large range of the SEI modulus values. A Student’s t-test yields a P-value of 0.00008, indicating that the decrease in modulus from the 3 cycle to 10 cycle samples is statistically significant. Further study is required to determine the cause of this change. Figure 5 illustrates the inhomogeneity in the modulus across the SEI surface. 625 μm² areas of the SEI layer are divided into 32 points (4 in the fast scan direction (horizontal) and 8 in the slow scan direction (perpendicular)). A single force curve is measured at each point and the modulus plotted as a function of position. Figure 5 is a grid from the 10-cycle sample, and the average modulus of the force curves plotted is 221 ± 112 MPa. The insets are two exemplary force curves corresponding to two force measurements within the grid. Specifically, the two insets have moduli of 490 MPa (top), and 28.0 MPa (bottom). Future NIB design will need to take into account the fact that the SEI layer can have a wide distribution of mechanical properties over a several hundred μm² area.

Several force curves, similar to the lower inset in Figure 5, initially exhibit a longer range of interaction between the probe and surface. The modulus of these curves is one to two orders of magnitude less than curves taken at points with a small range of interaction (top inset). The range of interaction for points with lower moduli is 35-300 nm, whereas for the higher moduli points the interaction distance is only 5-16 nm. We attribute this to the existence of a less reduced, less dense layer existing on top of a more reduced layer like that seen in the top inset. The less dense layer may be thicker and compression of this layer results in the longer range of interaction that is observed in the force curves. As the indentation of the surface continues, however, the softer layer is compressed and the force behavior resembles the curves with higher moduli. In the lower inset, this transition occurs when the applied force reaches 1.0 μN. Fitting the two slopes separately to Eq. (3) results in a modulus of 33.9 MPa ($R^2=0.938$) for the region below 1.0 μN and a modulus of 64.7 MPa ($R^2=0.984$) for the region above. The soft layer is observed on 74 of the total 350 curves. This could be an artifact of the half-cell construction; when the separator is removed the softer layer may peel off of the electrode. Zhang et al. reported a similar result in a beaker cell setup (no separator), and we are currently conducting experiments of this nature to determine the cause of this phenomenon.

Conclusions

This work demonstrates for the first time a quantitative assessment of the mechanical properties of the SEI layer that forms in NIBs. The results indicate that the SEI forms an inhomogeneous and at times bilayered structure, even on an inert electrode. The modulus we report can be incorporated into future mechanical studies that model the volume cycling of high capacity anode materials such as Sn, and the colloidal probe technique will be used to determine the mechanical properties of SEI formed by other electrolytes. The results will be correlated with NIB studies to elucidate the mechanism by which some electrolytes improve battery cycling performance. Additive compounds that decompose in a controlled manner or artificial SEI layers may offer an alternative strategy for mechanical confinement of the anode if conventional electrolytes do not produce a desirable structure. Future studies will make use of in-situ AFM setups to prevent peeling from the separator and collapse of

![Figure 3](image1.png)

**Figure 3** Force vs. separation curve fitted using the Hertzian model. Hundreds of force curves were analyzed using the Hertzian model. A representative force-separation curve is fitted in the linear region. The slope of the fit is proportional to the Young’s modulus as described by Eq. (3). Inset is an SEM image of the colloidal probe; the scale bar is 5 μm.

![Figure 4](image2.png)

**Figure 4** Histograms of SEI modulus measured using (a) 3 cycle and (b) 10 cycle samples.
a soft top layer if it forms. Additionally, this technique can be used to study full battery electrodes, complete with active materials and binders. Each component of the electrode would need to be probed separately to determine the individual mechanical properties. AFM techniques have been used to investigate the morphology, growth, and mechanical properties of the SEI in LIBs; it is pertinent, therefore, to apply these techniques to the emerging field of NIB research.

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References


Figure 5 Force mapping of SEI layer. 32 force profiles are measured within a 25 μm × 25 μm area. The Young’s modulus at each location in the grid is represented in a gradient scale. Two representative force profiles are shown in the insets. Exed out spaces correspond to anomalous data.
Nicholas Weadock received his B.Sc. in Materials Science and Engineering from the University of Maryland, College Park, in 2013. His research with Professor Liangbing Hu focused on sodium ion batteries with a specific interest in the formation and behavior of the solid electrolyte interphase. Some of his work was featured on NPR’s Morning Edition. He will pursue a PhD in Materials Science at the California Institute of Technology beginning fall 2013.

Nitinun Varongchayakul is a graduate student and researcher. She has a deep interest in nanotechnology and how single-molecule biomaterials behave mechanically. Nitinun holds a BEng in Nanotechnology from Chulalongkorn University, Thailand and MS in Materials Science and Engineering from University of Maryland at College Park, USA. Her Master’s research work with Professor Joonil Seog focused on nanomechanical force directed self-assembly of amyloid protein. She is currently a PhD student in Biomedical Engineering at Boston University, USA.

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Joonil Seog is an Assistant Professor of Materials Science and Engineering at the University of Maryland in College Park. His research interests include single molecule mechanics and nanomechanics of biological materials using high resolution force spectroscopy. He received a B.S. and M.S. degree in Chemical Technology from Seoul National University. He came to the United States in 1997, and received a Sc.D. degree in polymer science and technology from Massachusetts Institute of Technology (with Professor Alan J. Grodzinsky and Christine Ortiz) in 2003. He continued his work at Immune Disease Institute in Harvard Medical School as a postdoctoral fellow with Timothy A. Springer. Dr. Seog joined the UMD faculty as an Assistant Professor in 2007. His current research focuses on understanding mechanical properties of condensed DNA for gene delivery, nanomechanics of peptide based biomaterials and energy related materials.

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