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Employing nanoscale surface morphologies to improve interfacial adhesion between solid electrolytes and Li ion battery cathodes

Xin Su, Teng Zhang, Xin Liang, Huajian Gao, Brian W. Sheldon *

School of Engineering, Brown University, Providence, RI 02912, USA

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ABSTRACT

Solid state Li ion batteries are particularly susceptible to deleterious mechanical responses at interfaces, because the electrochemically driven volume changes must be accommodated by deformation of the solid electrolyte. In the current study, this was investigated with PEO electrolyte and V_2O_5 electrodes, using different morphologies (e.g. patterned films, plasma roughened surfaces, etc). Detailed finite element modeling of the experimental configuration was also used to analyze the results. Methods for improving the adhesion of this critical interface were also demonstrated. Relatively small improvements were attributed to plasma roughening. However, the introduction of large, thin sheets of material normal to the primary decohesion surface lead to unexpected large increases in the adhesive energy. For example, with patterned islands that were 800 nm tall, the increase in adhesion was approximately 8 times larger than the corresponding surface area increase. A finite element simulation of the decohesion process shows good agreement with the experimental values. Based on this analysis, it appears that thin elastic sheets in a much softer matrix can reduce stresses at the delamination front. This shielding effect provides a novel approach for improving the failure resistance of PEO electrolyte/V_2O_5 interfaces in solid state batteries.

1. Introduction

Solid state electrolytes in Li ion batteries are attractive for many applications because of their higher thermal and electrochemical stability compared to the liquid electrolytes that are widely used [1,2]. Polymer electrolytes offer important advantages such as mechanical flexibility (i.e., low elastic modulus), low costs, etc [3–12]. Poly ethylene oxide (PEO) has been widely investigated as a promising electrolyte for solid state batteries. Here, the electrochemical and mechanical properties of the interface between PEO and electrode materials are expected to be critical [6–9,13,14]. In particular, weak adhesion at these interfaces is likely to be problematic, however, systematic investigations of this behavior have not been previously reported.

Here we present a systematic study of adhesion between PEO electrolytes and vanadium oxide films. Extensive research has been conducted on developing vanadium oxides as cathode materials for lithium ion batteries [15–19]. For the current experiments, one important reason for using vanadium oxide as a model cathode is that it is relatively easy to produce in thin film form, compared to other multi-cation cathode materials. Lithium polymer batteries with vanadium pentoxide cathodes are also of interest for applications in electric vehicles, to reduce the safety risks associated with liquid electrolytes [20,21].

The baseline measurements that we report for PEO on vanadium oxide show relatively low adhesion energies between these materials. This weak interface with PEO is a serious issue, particularly because the cathode material undergoes substantial volume changes during Li insertion and removal. The impact of the resulting stresses at electrolyte/electrode interfaces requires careful consideration. With this in mind, both experiments and finite element method (FEM) simulations were used to understand the impact of surface morphology. It is well established that surface morphology can substantially impact adhesion of bimaterial interfaces [22–27]. A relatively simple example is a rougher surface that increases adhesion by increasing the effective interfacial contact area. Mechanisms that can lead to larger improvements are desirable, and one of the key finding in the work report here is that thin layers oriented perpendicular to the primary delamination front can substantially increase the adhesion energy. Overall, our results demonstrate that adjusting surface morphology of the electrode is an effective approach to improving the mechanical properties

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* Corresponding author at: 182 Hope Street, Providence, RI 02912, USA.
E-mail addresses: suxin81@gmail.com (X. Su), teng_zhang@brown.edu (T. Zhang), liangxin_matersci@126.com (X. Liang), huajian_gao@brown.edu (H. Gao), brian_sheldon@brown.edu (B.W. Sheldon).

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of the interface in vanadium oxide/PEO electrolyte system in solid-state lithium batteries.

2. Experimental and simulation section

2.1. Preparation of the V_2O_5 smooth film and patterned film

The current collector 100 nm Ti/100 nm Au was first deposited on quartz substrates (25.4 μm in diameter and 250 μm in thickness, University wafer) by electron-beam evaporation. The 50 nm V_2O_5 film was then deposited on the current collector by magnetic sputtering (Lesker lab 18) with a vanadium target in an atmosphere of 90% Ar and 10% O_2. This process produced amorphous films. The oxygen contents were not measured, but are believed to contain less than the stoichiometric oxygen level.

The patterned films were produced through a standard lithographic process. Photoresist (AZ 5214 E) was spin coated on the current collector at a rate of 1500 rpm for 45 s. Then the photoresist was baked at 110 °C for 60 s. After baking, the photoresist was exposed with 365 nm wavelength (80 mJ/cm^2 dose), using the 2000 LPI fine Ni Mesh as the mask (with patterned size of 7 μm × 7 μm). The sample was developed in AZ 300 MIF for 70 s. Finally the V_2O_5 patterned films with islands of different heights were created by magnetic sputtering and removing the photo-patterned.

2.2. O_2 plasma treatment and annealing process

The as deposited vanadium oxide film were treated by oxygen plasma at 200 W for 5 min and annealed at 400 °C in air for 8 h to investigate the impacts of plasma and annealing treatments on the adhesive energy between the PEO electrolyte and the film. The as-deposited vanadium oxide patterned films were also treated by these two approaches to see their impacts on the adhesion energy between the PEO electrolyte and the patterned films.

2.3. PEO electrolyte films

The 1.67 g PEO electrolyte (Medtronic Inc.) was first dissolved in 10 g acetonitrile (Sigma–Aldrich). The solution was spin coated on V_2O_5 smooth films and patterned films at a rate of 700 rpm for 90 s. After drying at room temperature, the 5.9 μm PEO electrolyte films were firmly attached to the V_2O_5 films.

2.4. Peeling test

The PEO electrolyte films on vanadium oxide were peeled off using an Instron 5882 with a force resolution of 1 mN. Part of the PEO electrolyte was first manually peeled off and attached to an adhesive tape with quick dry glue, and the remaining PEO film was then peeled off at a constant rate of 0.7 mm/min. An angle of ~90° was maintained between the force direction and interface during the peeling test. The force needed to peel the PEO electrolyte film from the vanadium oxide film was recorded and used to calculate the adhesion energy between PEO electrolyte and the vanadium oxide films.

2.5. Characterization of V_2O_5 films' surface morphology and Au film

The surface morphologies of V_2O_5 smooth films and patterned films before/after annealing and plasma treatment were characterized by scanning electron microscopy (SEM, Zeiss LEO-1530 VP at 10 kV) and atomic force microscopy under tapping mode (AFM, Asylum MFP-3D Origin AFM). The crystal structure of V_2O_5 smooth film before/after annealing was characterized by X-ray Diffraction (XRD Siemens D-5000) from 10° to 90° at glancing angle of 1° and scan rate of 0.02°/s. The surface modification on Au film during the photolithography process was characterized by X-ray Photoelectron Spectra (XPS, Physical Electronics Quantum 2000) at 100 W and 18 kV.

2.6. Nanoindentation of PEO

The Young's modulus of the spin coated PEO electrolyte on V_2O_5 was determined with a Triboindenter (Hysitron), using Berkovich indenter, the load control mode, the maximum load of 10 μN and loading/unloading rate of 4 μN/s. The indentation tests were performed with/without 2 s pause. The Young's modulus were similar with/without pause, which were obtained from Triboscan software Analysis of Hysitron TI950. The shape of the indentation curves shows that there is some rate dependent deformation of the PEO (Fig. S5). This was not accounted for in the initial simulations that are reported here.

2.7. Finite element model

The system of PEO attached to the flat and patterned V_2O_5 substrates was simulated with a finite element model (FEM). In the numerical simulation, a three-dimensional (3D) strip and a thin plate with symmetry boundary condition on the lateral sides are used to represent the unit cell of PEO and V_2O_5 substrate with periodical islands, respectively. Since full 3D FEM simulations for the PEO-island system require large scale computations, here we adopt a smaller square island with width of 2 μm (shown in Fig. S4(a)), while keep the area ratio of the island the same as the experimental set up (~25%). A symmetry boundary condition is applied to the right end surface of both the PEO and V_2O_5 to prevent crack nucleation from the right end of the strip due to the modulus mismatch. These boundaries will lead to $\varepsilon_{zz} = 0$ and a close zero value of ε_{xx} at the position far away from the interfacial crack tip. The composite structure contains an initial edge crack along the interface between PEO and V_2O_5. A constant velocity loading is applied on the top surface of the PEO strip where a very low loading rate is adopted to ensure a quasistatic process. All the 3D FEM simulations are performed with ABAQUS/Explicit. Both the PEO and V_2O_5 are modeled using 8-node linear brick elements with incompatible modes (C3D8I). The PEO and V_2O_5 are modeled as linear elastic materials with geometrically nonlinear deformation, Poisson's ratio of 0.3, and Young's modulus of 0.85 GPa and 100 GPa, respectively. The adhesion between PEO and V_2O_5 substrate is described with cohesive elements implemented in ABAQUS. A triangular softening cohesive law with a maximum strength and separation distance at 85 MPa and 80 nm is used to describe the interaction between PEO and V_2O_5 substrate for both flat and rough interface (illustrated in Fig. S4(b)). The damage initiation of cohesive interaction is described with quadratic nominal stress criterion (shown in Eq. (S2)) so that the decohesion in normal and shear directions follow the same traction-separation law and will equally contribute to the failure under mix mode loading.

3. Adhesion results

Fig. 1(a) and (b) show the 90° peeling test results for PEO removal from the vanadium oxide film at rates of 0.7 mm/min and 1.4 mm/min. These results indicate that the peeling rate has no impact on the applied peeling force. This constant peeling force demonstrates the uniformity of the interface between V_2O_5 film and PEO electrolyte. Here the adhesion energy 3.2 J/m^{2}of PEO to the V_2O_5 is calculated from the measured peeling force. As shown in Fig. 2(a)–(c), the surface morphology of the smooth V_2O_5 film is