

Supporting Information

Deformation and Chemomechanical Degradation at Solid Electrolyte – Electrode Interfaces

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Methods

Preparation of V_2O_{5-x} film on quartz substrate

The 100 nm Ti / 100 nm Au current collector was deposited on quartz glass substrates (1 inch in diameter and 250 μ m in thickness, University wafer) by electron-beam evaporation. The 50 nm V_2O_{5-x} 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 produces amorphous films that are oxygen deficient (denoted with the subscript 5-X).

Characterization of V_2O_{5-x} film as prepared

The surface morphologies of V_2O_{5-x} films and patterned films were characterized by scanning electron microscopy (SEM, Zeiss LEO-1530 VP at 10 kV). The crystal structure of V_2O_{5-x} film 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.

Peeling test of PEO electrolyte loaded on V_2O_{5-x} film before/after cycling

The PEO electrolyte film that was produced on the V_2O_{5-x} film before/after the battery tests, was peeled off (Instron 5882, 500 N load cell with force accuracy of 1 mN). Part of the PEO film was firstly manually debonded at an edge, and attached to adhesive tape with quick dry glue. The remaining of PEO film was then peeled off at a constant rate of 0.7 mm/minute. The measurement is custom designed to maintain a peeling angle of $\sim 90^\circ$ between the force direction and the interface

during the test. The force needed to peel the PEO electrolyte film from the V_2O_{5-x} film was recorded and used to determine the adhesion energy between PEO electrolyte and the V_2O_{5-x} film.

Battery and impedance measurement of V_2O_{5-x} film in liquid and PEO electrolytes

The battery cell of V_2O_{5-x} film (50 nm) in liquid electrolyte (lithium bis(trifluoromethanesulfonyl)imide in tetraglyme) and PEO electrolyte (mixture of lithium bis(trifluoromethanesulfonyl)imide, tetraglyme and PEO, 220 μm), which was prepared by slurry laminate, was assembled according to Figure 1 (a) and (b). The cell for V_2O_{5-x} film in PEO electrolyte was baked at 60°C for 2 h before the battery and impedance tests to improve the wetting conditions of interfaces in the sandwich structure of V_2O_{5-x} film/PEO electrolyte arrays/lithium foil. The battery cells for V_2O_{5-x} film in liquid electrolyte and PEO electrolyte were both performed at room temperature. The V_2O_{5-x} film was used as working electrode. Lithium foil was used as counter/reference electrode. These cells were galvanostatically cycled between 4 V and 2 V at the current of 1 μA using Arbin Instruments BT2000. The impedance measurements were performed in a two-electrode configuration at open-circuit voltage with frequency ranging from 100 mHz to 100 KHz using Biologic VSP. These data were then fit with an appropriate equivalent circuit using ZView software (Scribner Associates Inc.).

In-situ stress measurement of V_2O_{5-x} film in liquid/PEO electrolytes during electrochemical cycling

Stress evolution in the V_2O_{5-x} films in different electrolytes were measured *in situ* by a multi-beam optical stress sensor (MOSS). This technique has been used previously to measure internal

stresses in thin films electrode during lithiation and delithiation.¹⁻³ In general, the internal stress generated in a thin film produces curvature changes ($\Delta\kappa$) in the thin film-substrate system (here, the V_2O_{5-x} /current collector layer is the thin film and quartz is the substrate). These small curvature changes are monitored in-situ during the tests. If the underlying elastic substrate (i.e., quartz) is fully free to bend, the measured curvature change is proportional to the product of the film thickness, h , and the average stress (through the thickness of the film), $\langle\sigma\rangle$, via the Stoney equation⁴:

$$\langle\sigma\rangle h = \int_0^h \sigma(z) dz = \frac{M_s h_s^2 \Delta\kappa}{6} = F_{nom}(\Delta\kappa) \quad (1)$$

where h_s and M_s are the thickness and biaxial modulus of the substrate (87.95 GPa for quartz), respectively. By convention, negative curvature values correspond to compressive stress in the film.

In previous work with liquid electrolytes where the bending of the film-substrate system is effectively unconstrained, Equation (1) provides a direct measure of $\langle\sigma\rangle$ if h is known (corrected versions of Equation (1) are also available for larger values of h [32]). For the limiting case in Equation (1) where $h \ll h_s$, it is sometime convenient to equate the stress-thickness product to a “membrane force” on the substrate surface that is produced by the stress in the film, $f = \langle\sigma\rangle h$ (i.e., with dimensions of force per length). With the solid electrolyte that is present in our experiments, the substrate should still bend in response to f , but Equation (1) is no longer valid. With this in mind, the experimental measurements are reported as the nominal force, $F_{nom}(\Delta\kappa)$ that appears on the far right hand side of Equation (1). As noted above, direct

application of Eq. (1) where $F_{nom} = \langle \sigma \rangle h$ is only valid for the baseline measurements that we made with a liquid electrolyte. With the solid electrolyte, the same membrane force f is applied by the film, but the measured quantity $F_{nom}(\Delta\kappa)$ is reduced because the substrate bending is constrained, as noted above. In this case, the relationship between $F_{nom}(\Delta\kappa)$ and f was obtained by the finite element analysis described below.

Finite element model of thin film bending with a solid electrolyte

The thin film-substrate system depicted in Figure 1 was simulated using finite element method (FEM). As shown in Figure 4(a), a three-dimensional (3D) circular thin plate with a diameter of 1 inch was divided into three parts along the thickness direction to represent Quartz substrate, V_2O_{5-x} thin film, and PEO electrolyte with thicknesses of 250 μm , 50 nm, and 220 μm , respectively. The bottom surface of PEO electrolyte is fixed in the model since the deformation of Li foil is negligible compared to that of PEO electrolyte. In the experiment, one side of the quartz/PEO thin-film is clamped with the current collector belt, so we fixed one edge of the plate in the FEM model as well. Curvature changes were measured on the center of the sample in both MOSS experiments and FEM simulations. An analogy between thermal expansion and volume change of V_2O_{5-x} upon lithiation / delithiation cycles is used in FEM simulations. All the FEM simulations were performed with commercial finite element code ABAQUS and 20-node quadratic hexahedral elements with reduced integration (C3D20R) were used for the entire mesh. FEM made it possible to quantitatively interpret the F_{nom} values that were obtained during the *in situ* MOSS measurements.

Reference:

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- (4) Su, X.; Viste, M.; Hossick-Schott, J.; Yang, L.; Sheldon, B. W.: In-Situ Stress Measurement during Heat Treatment of Amorphous Tantalum Oxide. *ECS Journal of Solid State Science and Technology* **2015**, *4*, N64-N69.

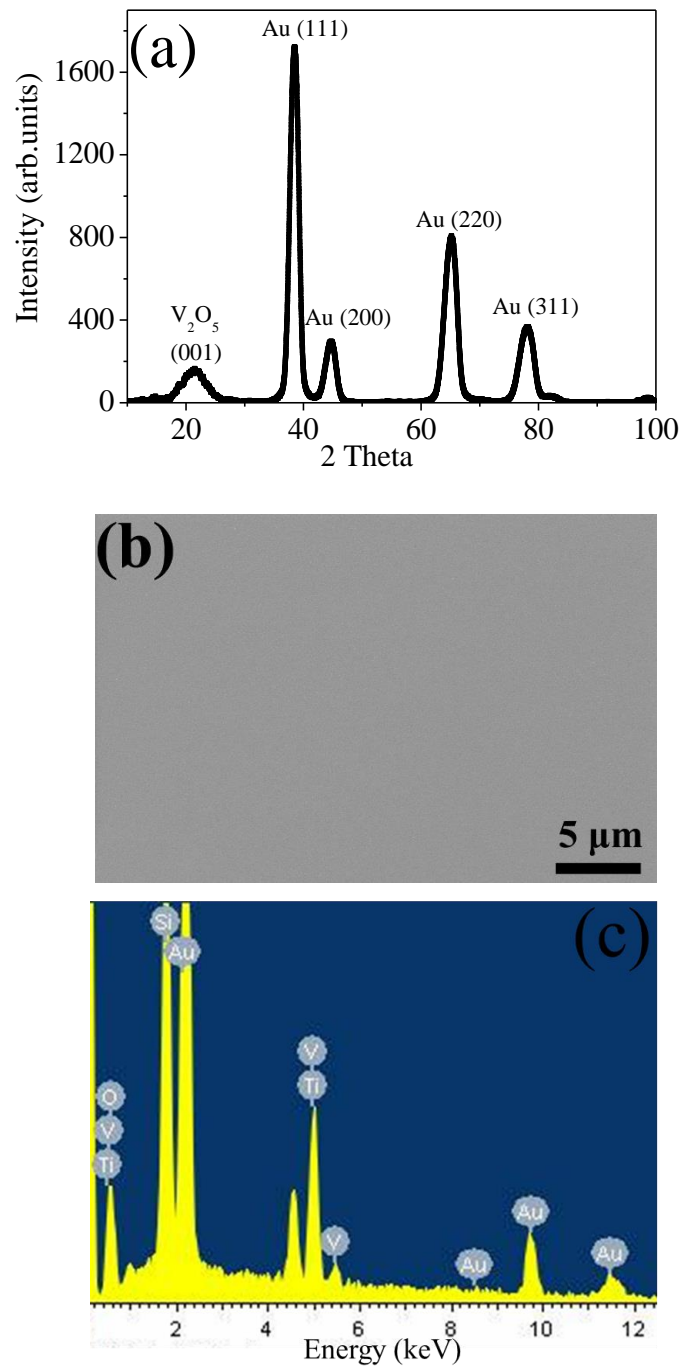


Figure S1. The XRD (PDF number:089-0611) (a), SEM (b) and EDS (c) of 50 nm V_2O_{5-x} film deposited on the current collector of 100 nm Au/100 nm Ti.

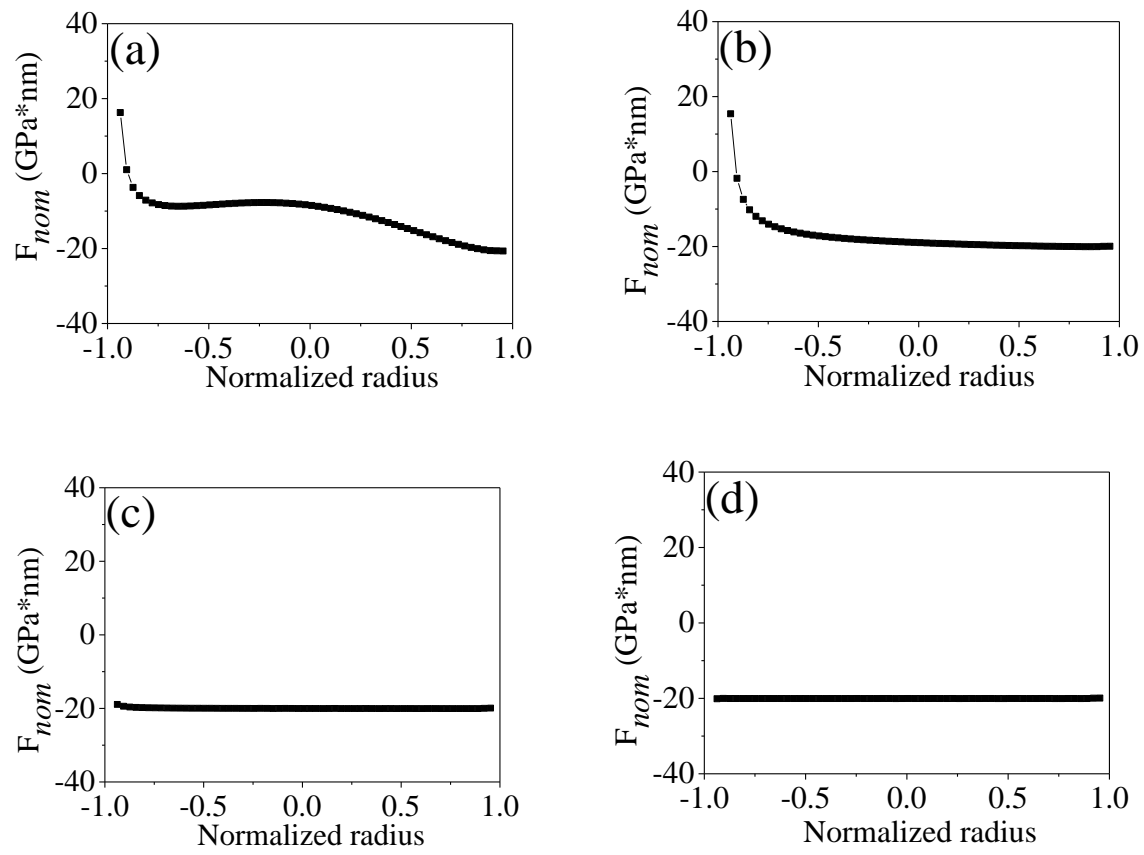


Figure S2. Stress-thickness distribution along radial direction in PEO electrolyte with effective modulus of 10000 Pa (a), 100 Pa (b), 1Pa (c) and in liquid electrolyte (d). The left end of the curve is the fixed point of the sample.