

# Mechanisms of the Cyclic (de)lithiation of $\text{RuO}_2$

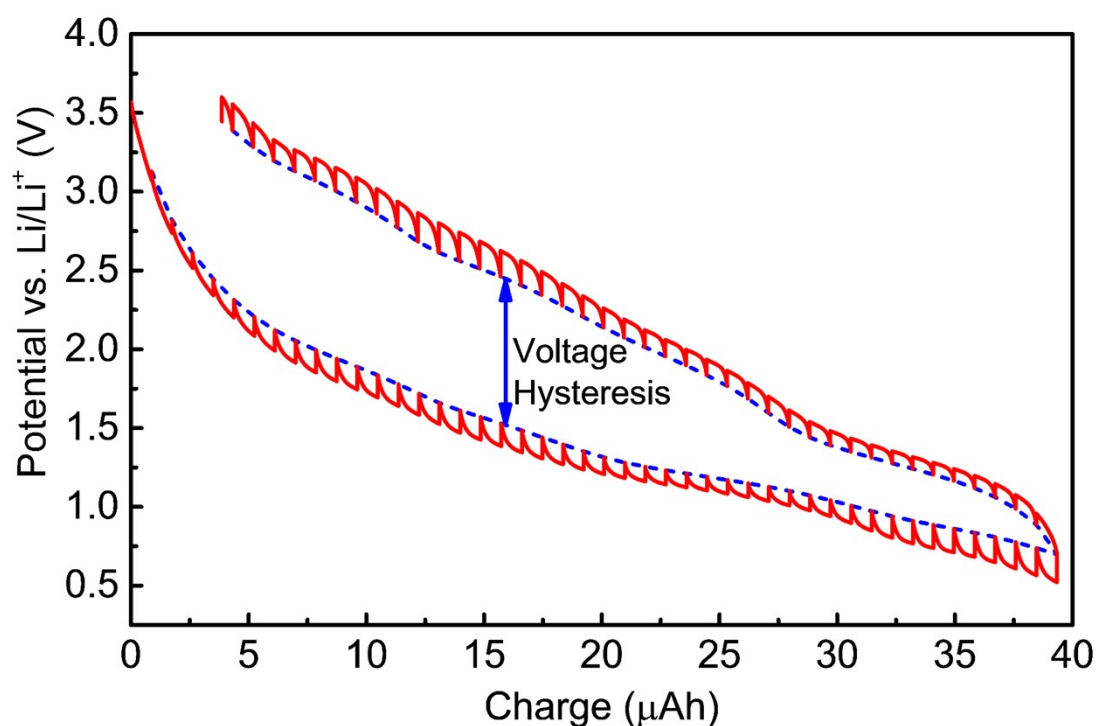
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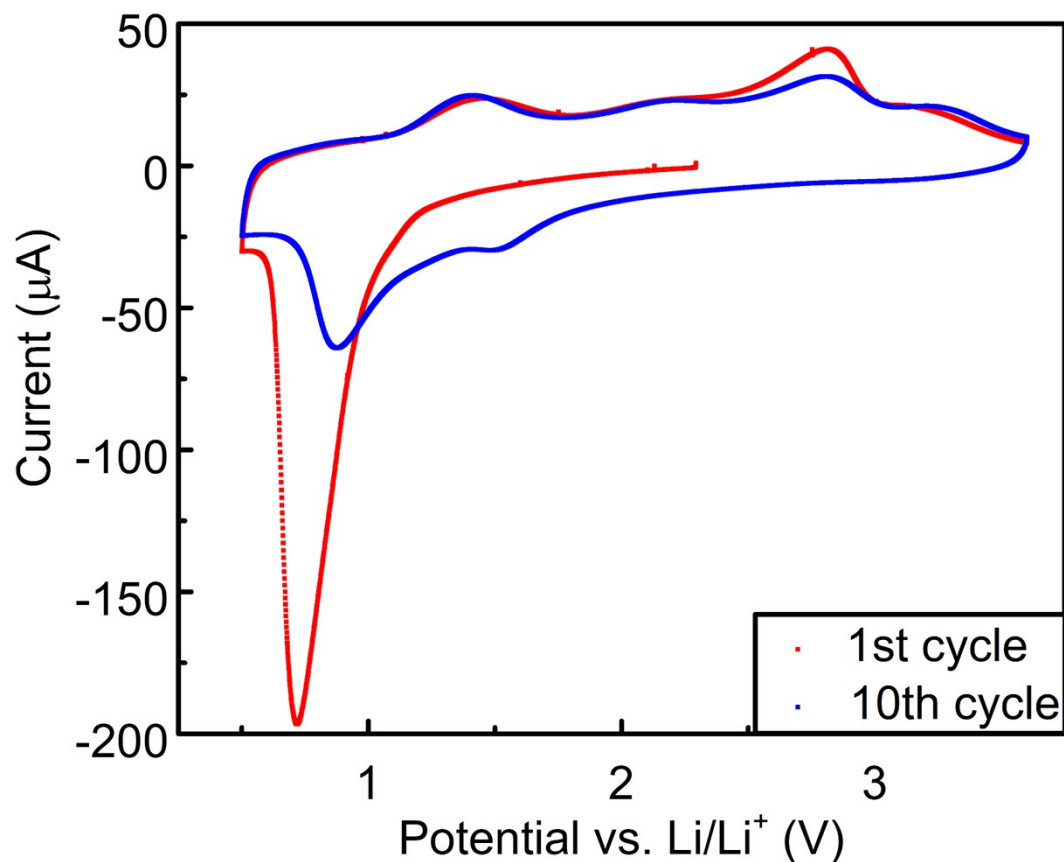
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## Voltage hysteresis of $\text{RuO}_2$



**Figure S1.** Galvanostatic iterative titration for a  $\text{RuO}_2/\text{LiPF}_6/\text{Li}$  cell obtained at a scan rate of 3.5  $\mu\text{A}$  (1 C) between 0.5 V and 3.6 V. The step size was 15 min and the relaxation time was 1.5 hours.

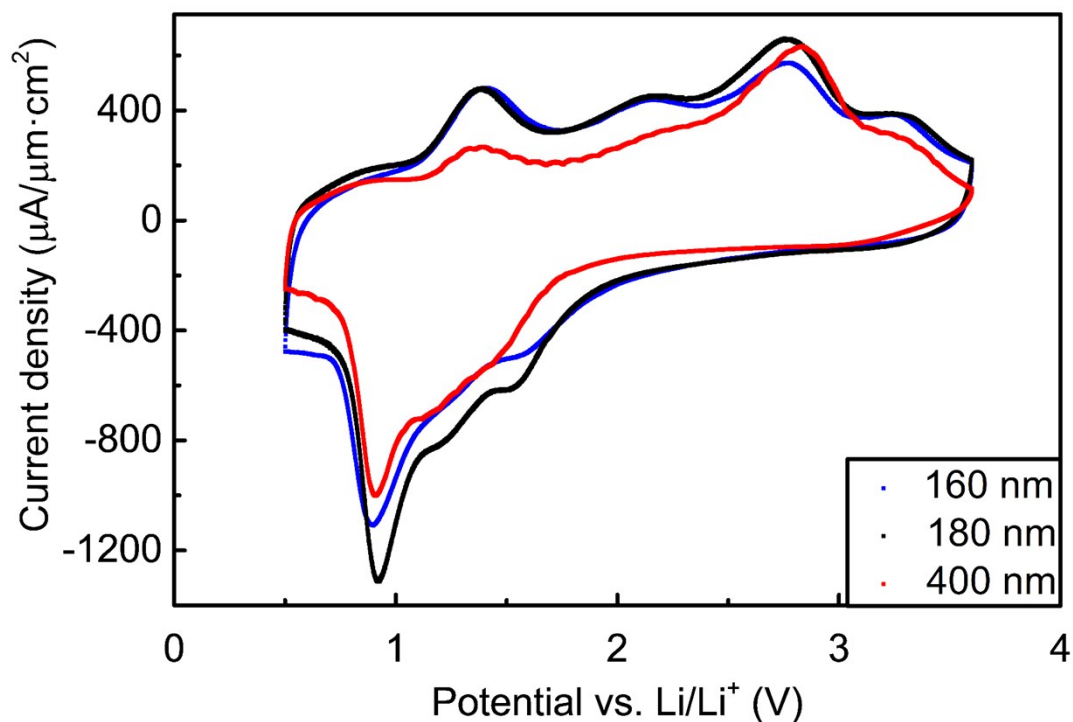
## Differences between 1<sup>st</sup> cycle CV and stable CV



**Figure S2.** Cyclic voltammograms during 1<sup>st</sup> cycle and 10<sup>th</sup> cycle of a RuO<sub>2</sub>/LiPF<sub>6</sub>/Li cell, obtained at a scan rate of 0.5 mV/s between 0.6 V and 3.6 V.

As can be seen in Fig. S2, the CV for the 10<sup>th</sup> cycle (stable cycle) is very different from the CV for the 1<sup>st</sup> cycle, which indicates that different chemical processes happen in cycles subsequent to the 1<sup>st</sup> cycle. Therefore, studying cycles beyond the 1<sup>st</sup> cycle is essential to understand the behavior of RuO<sub>2</sub> during cycling.

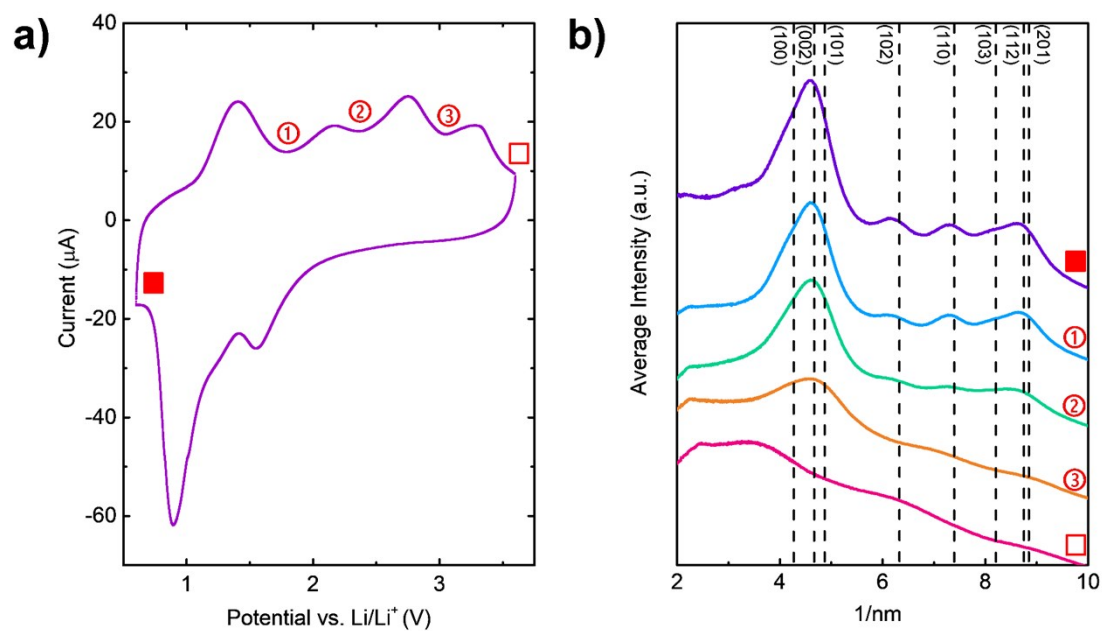
### CV of RuO<sub>2</sub> thin films with different thicknesses



**Figure S3.** CV curves for three RuO<sub>2</sub> thin film samples with different thicknesses at a scan rate of 0.5 mV/s between 0.5 V and 3.6 V.

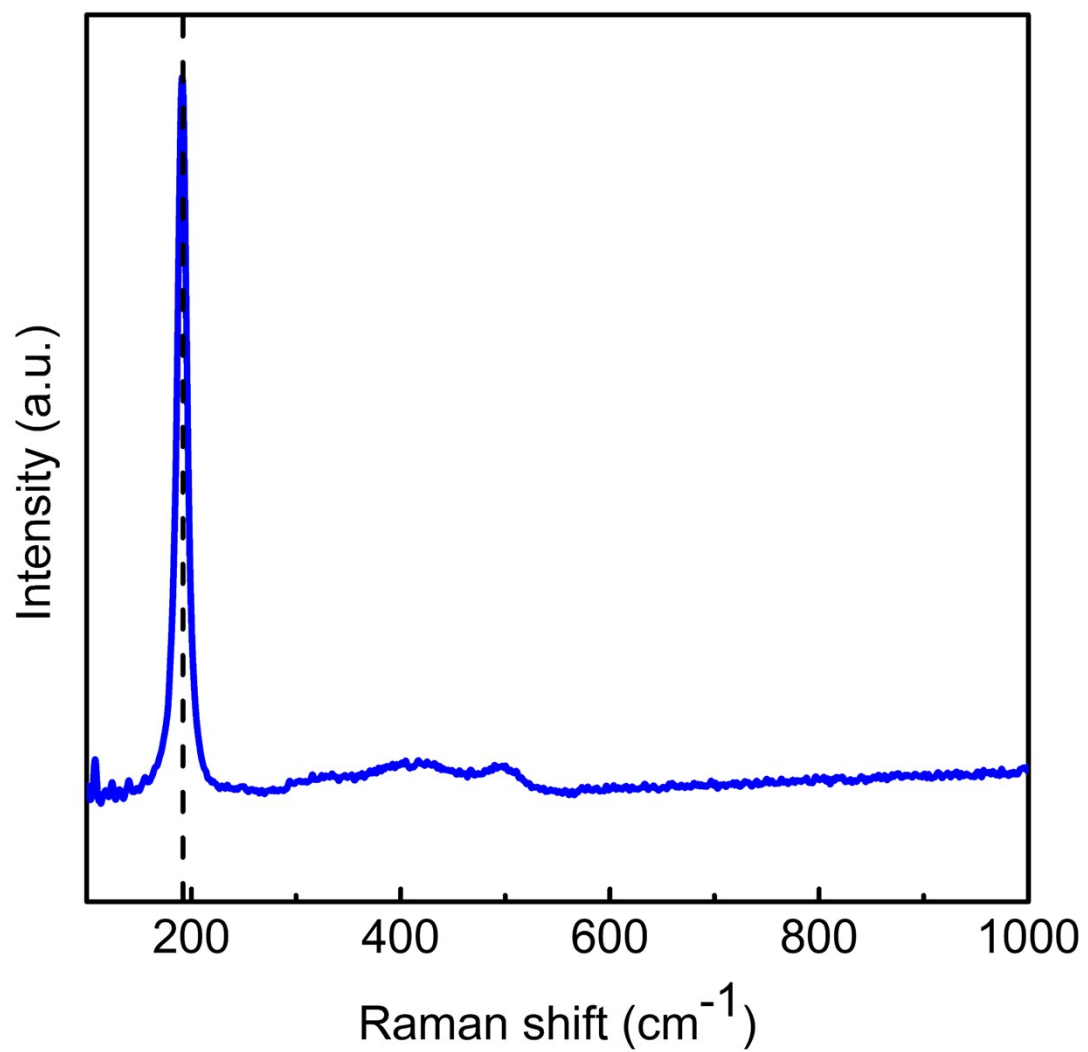
CV results for RuO<sub>2</sub> samples with different thicknesses showed little voltage shift (~50 mV) for the conversion reaction although the thickness of the thickest sample was more than twice that of the thinnest sample. This behavior implies that long-range diffusion of Li was not the rate-limiting step in the conversion reaction.

## Transmission electron diffraction patterns



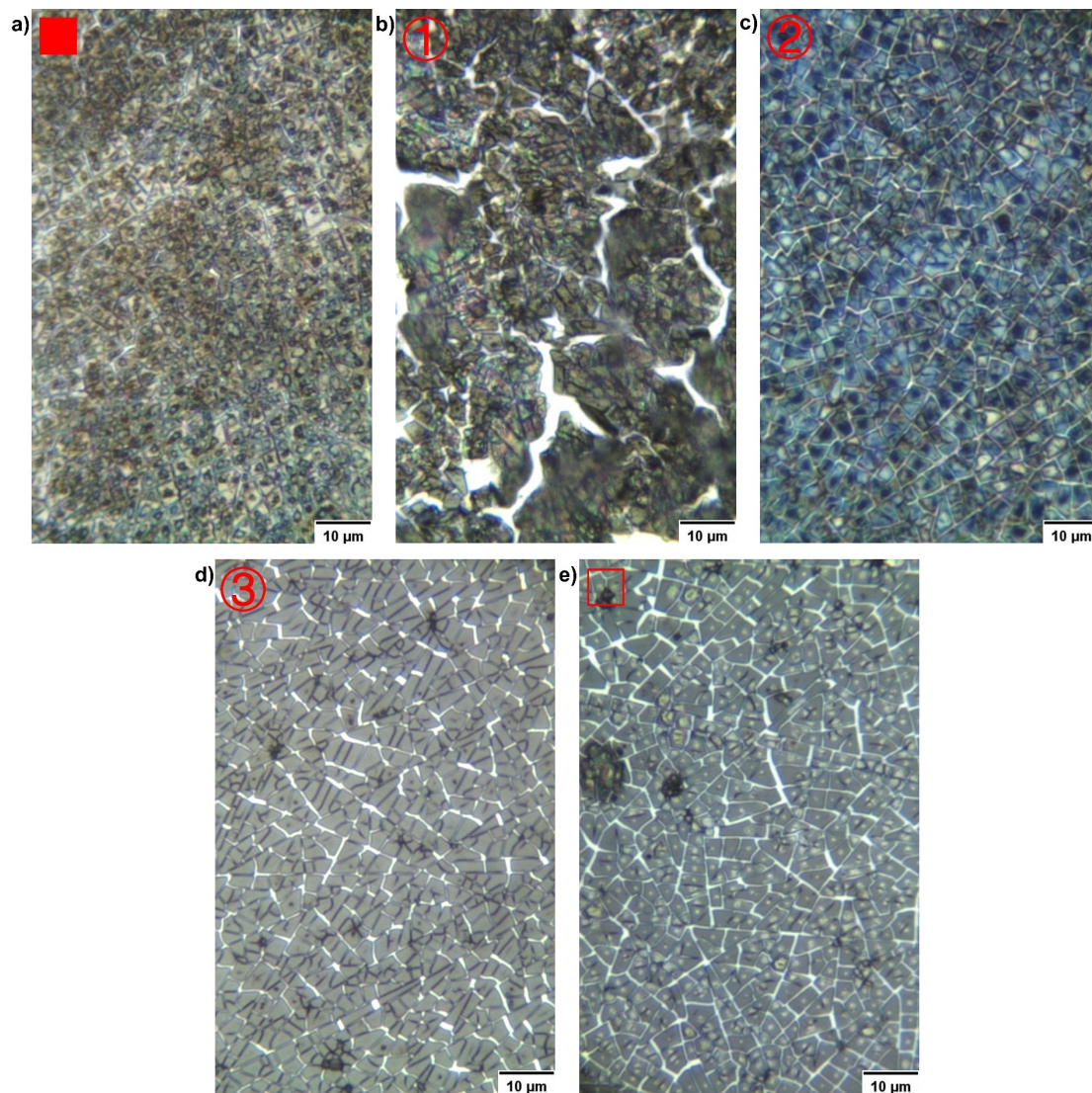
**Figure S4.** (a) Different  $\text{RuO}_2$  films were delithiated to different states ( $\blacksquare$ , ①, ②, ③ and  $\square$ ) for ex situ transmission electron diffraction analysis. (b) Radial average intensities of electron diffraction patterns. Dashed lines show the position of peaks expected for different crystal planes of Ru.

## Raman spectrum of single crystal Ru



**Figure S5.** Raman spectrum for a 10 nm-thick single crystal Ru film.

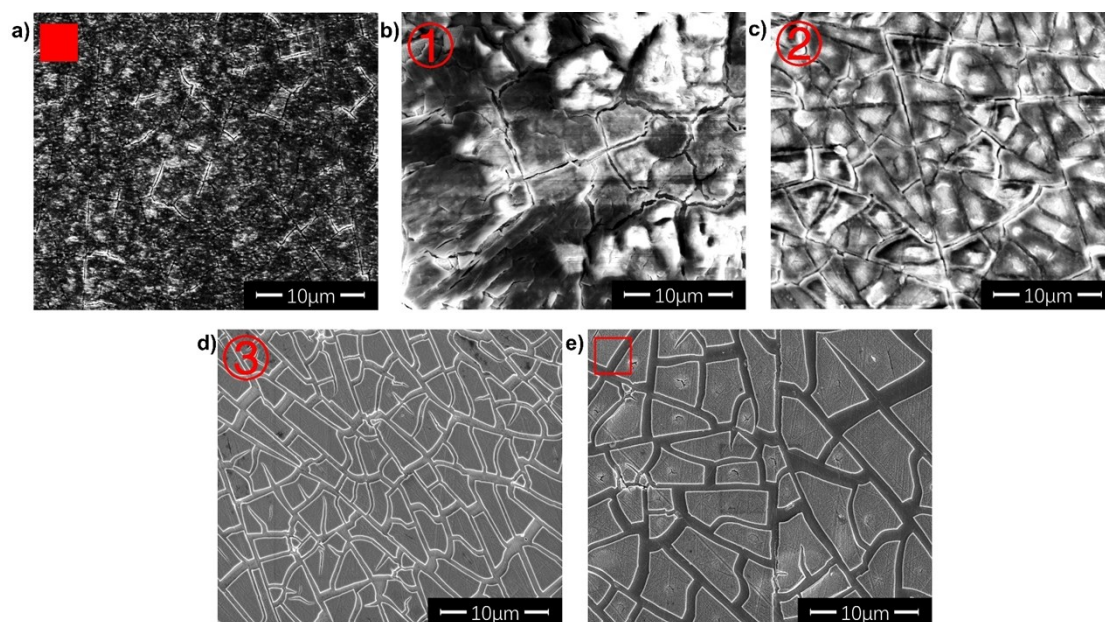
## Optical microscope images



**Figure S6.** (a) Surface of a fully lithiated sample (■) imaged using an optical microscope. (b)-(d) Surface of samples delithiated to ①-③. (e) Surface of a fully delithiated sample (□).

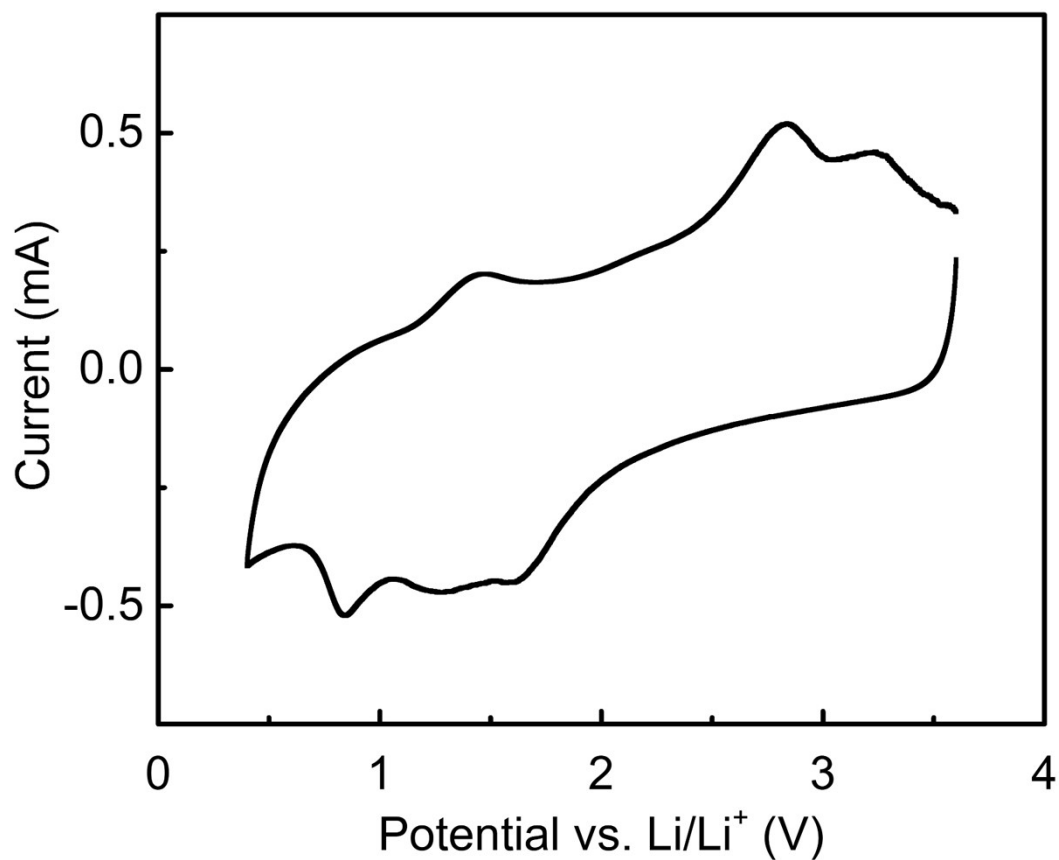


## SEM images



**Figure S7.** (a) Surface of a fully delithiated sample (■) imaged using an SEM. (b)-(d) Surfaces of samples delithiated to ①-③. (e) Surface of a fully delithiated sample (□). The average spacing between islands for sample ③ and sample □ is similar. The two pictures were taken from different areas.

## CV for powder-based RuO<sub>2</sub> Electrodes

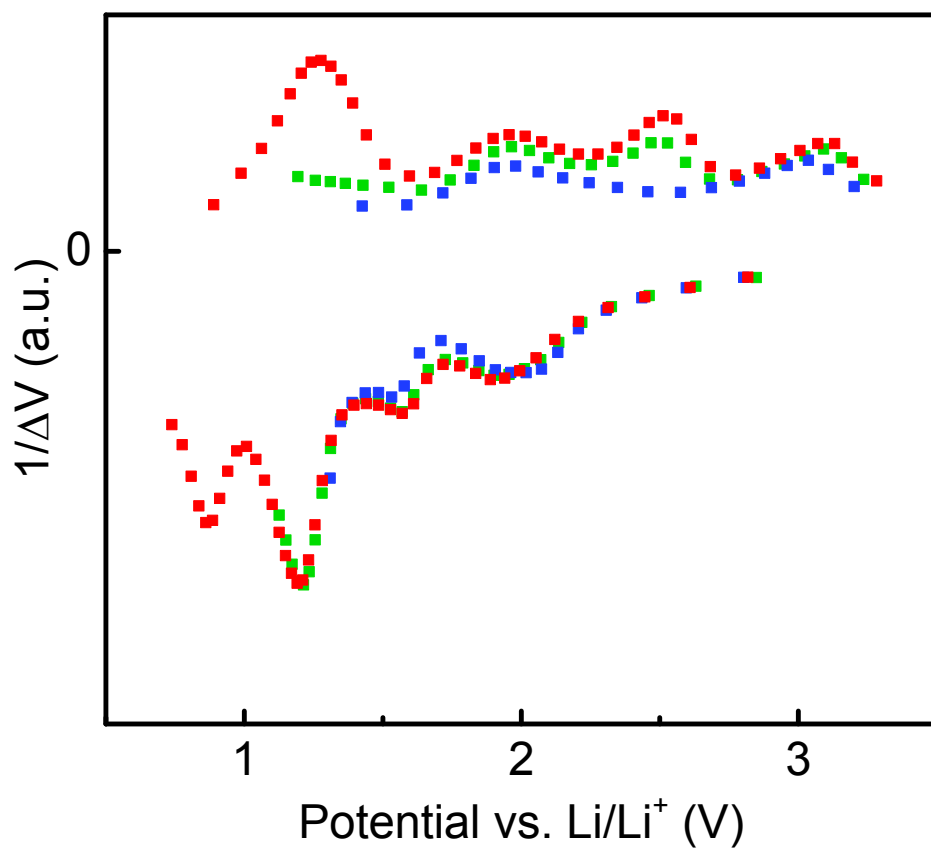


**Figure S8.** Cyclic voltammogram for the second cycle of a powder-based RuO<sub>2</sub> electrode in a RuO<sub>2</sub>/LiPF<sub>6</sub>/Li cell obtained at a scan rate of 0.5 mV/s between 0.6 V and 3.6 V.

To determine if our analysis based on studies of thin films could also be applied to reactions in powder-based RuO<sub>2</sub> electrodes, we also did CV tests for powder-based RuO<sub>2</sub> electrodes, and the cyclic voltammogram for one full cycle is shown in Figure S8. As can be seen in the figure, although the magnitudes of the peaks are different from the thin film samples, the positions are similar, indicating that similar reactions occurred in the powder-based electrodes.

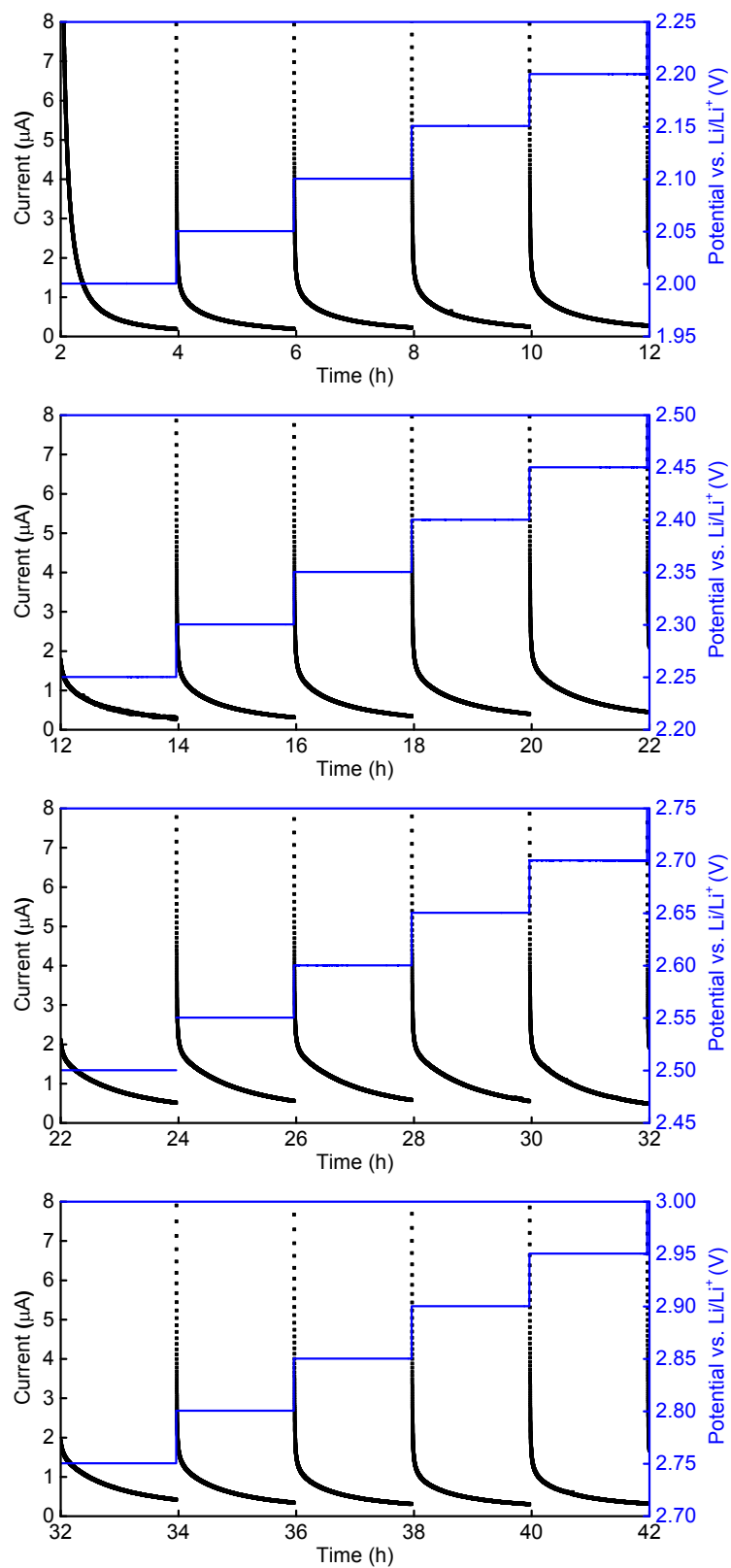


## GITT with Different Lower Cutoff Voltages



**Figure S9.**  $1/\Delta V$  vs. voltage curve extracted from GITT tests of a  $\text{RuO}_2/\text{LiPF}_6/\text{Li}$  cell with different lower cutoff voltages.

## Complete Data of PITT Test



**Figure S10.** Current and voltage as a function of time during a PITT test of a  $\text{RuO}_2/\text{LiPF}_6/\text{Li}$  cell. The steps shown are from 2.0 V to 2.95 V, with a step size of 50 mV.