

Supporting Information:

Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO₂
(Anatase) Nanoparticles

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Electrochemical Impedance Spectroscopy of TiO₂ Nanoparticle Films

A. Experimental Methods. Electrochemical Impedance Spectroscopy (EIS) was performed on nanostructured TiO₂ films made with 7 nm and 10 nm size particles. The impedance measurements were carried out using a Solartron 1252 in the frequency range from 100 kHz to 0.1 Hz, and the amplitude of the ac signal was controlled at 10 mV. The EIS measurements were performed with a dc bias at 1.5 V and 1.75 V vs Li/Li⁺. The experimental spectra were modeled numerically using the ZView equivalent circuit fitting program.

B. Results and Discussion. The primary objective of the EIS experiments is to further investigate the interfacial behavior of our TiO₂ films and to gain additional insight concerning the double layer and pseudocapacitance contributions to the electrochemical

capacitance. Figure S1 shows the potential-dependent impedance spectra for the nanostructured TiO₂ electrodes. The spectra were analyzed using an equivalent circuit model (shown in Fig. S2) which describes the electrochemical impedance behavior for the nanostructured TiO₂ films.¹ In the frequency range below 10 Hz, the impedance is dominated by the constant phase element, CPE_{echem}, in parallel with a resistance, R_{leak}. The CPE_{echem} represents the electrochemical capacitance of a porous electrode, and the R_{leak} in parallel signifies a small leakage current at the electrode/electrolyte interface.¹

We used numerical fitting of the equivalent circuit model to determine capacitance values for the films made with 7 nm and 10 nm nanoparticles at two different potentials (see Table S1). The results indicate that at the same potential, films prepared from 7 nm nanoparticles possess higher levels of capacitance than films prepared with 10 nm anatase nanoparticles. This response occurs regardless of whether the current is predominantly from capacitive processes (at 1.50 V) or if there is a significant contribution from intercalation (at 1.75 V). Such behavior is consistent with the voltammetry results shown in Fig. 7 and the additional analysis in Fig. 8. It is also interesting to note that for a given film, the magnitude of the capacitance does not vary too much as a function of potential. This feature is also evident in the voltammetry shown in Fig. 7.

Table S1: Dependence of the specific capacitance on particle sizes and applied potentials

	1.75 V	1.50 V
C _{echem} . for 7 nm TiO ₂ (F)	1.1 mF	1.6 mF
C _{echem} . for 10 nm TiO ₂ (F)	0.9 mF	0.9 mF

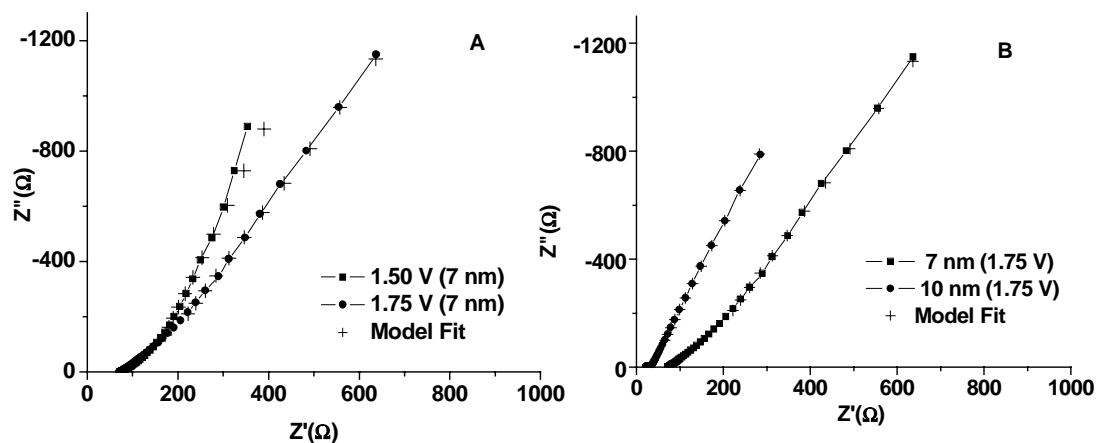


Figure S1. Nyquist representation of the frequency dispersion (0.1 Hz to 100 kHz) for TiO_2 films made with 7 nm and 10 nm nanoparticles. A) The impedance response for 7 nm film at 1.50 V and 1.75 V vs Li/Li^+ . B) Comparison of the impedance behavior for the 7 nm and 10 nm films at 1.75 V vs Li/Li^+ . Fit of the equivalent circuit model (Fig. S2) for each data set has been overlaid on the respective plots.

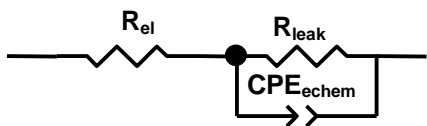


Figure S2. Equivalent circuit model that describes the electrochemical impedance behavior for nanostructured TiO_2 electrodes in nonaqueous electrolytes.

Reference

- (1) Miller, J. M.; Dunn, B. *Langmuir* **1999**, *15*, 799.