Supporting Information

Surface State Recombination and Passivation in Nanocrystalline TiO₂ Dye-Sensitized Solar Cells

Alexander R. Pascoe[†], Laure Bourgeois[‡], Noel W. Duffy[§], Wanchun Xiang[†] and Yi-Bing Cheng^{†*}.

⁺ Department of Materials Engineering, Monash University, Victoria 3800, Australia

^{*} Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia

§ CSIRO Energy Technology, Clayton, Victoria 3169, Australia

Impedance and IMVS measurements



Figure S1. Equivalent circuit used for the impedance modeling. R_s represents the series resistance which describes the impedance of the metal contacts. R_r and C_{μ} represent the recombination resistance and chemical capacitance respectively, which describe the charge transfer resistance and charge separation at the film/electrolyte interface. Z_W represents the Warburg impedance, which describes the diffusion of the electrolyte species between the photoanode and the counter-electrode. R_{Pt} and C_{Pt} represent the counter electrode resistance and charge transfer and charge transfer and the counter-electrode.

The equivalent circuit used to fit the impedance data is shown in Figure S1, and representative spectra of the impedance data are shown in Figure S2. The accuracy of experimental data derived from impedance measurements is limited by the accuracy of the equivalent circuit model, as well as the ability to differentiate between the responses of each circuit element. As seen in the typical impedance spectra, the impedance response of the transport resistance element was not observed at most of the applied potentials due to the overlapping response of the counter-electrode impedance. For this reason the transport component was not included in the applied equivalent circuit. At the more positive potentials (Figure S2a), it is difficult to distinguish between the impedance responses originating from the TiO₂/electrolyte interface and the counterelectrode. This overlap in the impedance responses introduces uncertainty into the modeling of the impedance data. It is not until there is an observed separation between the two circles (Figure S2b) that we can have a greater degree of confidence in the calculated values for each equivalent circuit element. The overlap of the elemental responses is once again seen at the more negative applied potentials shown in Figure S2d. In this impedance spectrum, the impedance responses from the TiO_2 /electrolyte interface, the electrolyte diffusion and the counter-electrode are all clearly identifiable, however there is considerable overlap between all three regions which means that the modelling of the individual circuit elements is not as precise as the middle potentials (Figure S2c).



Figure S2. Typical impedance spectra for four different applied potentials. (a) Impedance spectrum measured at -600mV. The impedance responses of the TiO_2 /electrolyte circle and the counter-electrode circle are difficult to distinguish. (b) Impedance spectrum measured at -620mV. A noticeable separation is observed between the high frequency counter-electrode response, and the mid-frequency TiO_2 /electrolyte circle. (c) Impedance spectrum measured at -700mV. The spectrum is dominated by the mid-frequency TiO_2 /electrolyte circle, and a small counter-electrode circle is seen at high-frequencies. (d) Impedance spectrum measured at -900mV. The high-frequency counter-electrode response, the mid-frequency TiO_2 /electrolyte response and the Warburg impedance are all observed in this spectrum, however there is considerable overlap between the circuit element responses.

A typical IMVS spectrum is shown in Figure S3. As discussed in previous literature,¹⁻³ IMVS measurements show a semicircular response in a plot of the imaginary and real photovoltage. We used a semicircular fit of the experimental data to calculate the frequency at the peak of the response. This value was then used to calculate the electron lifetime in accordance with the previously published theory.¹⁻³



Figure S3. Typical IMVS spectra. Data points are shown in the red circles and the fit is shown by the solid red line.

There appeared to be a good agreement between the impedance lifetime data and the IMVS lifetime data at the middle and more positive potentials. At the more negative potentials the IMVS data and the impedance data diverge. The IMVS data was considered to be more reliable at the more negative potentials and the more positive potentials because of the problems with overlapping impedance responses. For this reason, the IMVS data was afforded more weight when applying the electron transfer model to the experimental results.

Interpretation of previous experimental charge transfer rate

If the electron transfer rate is proportional to the reactive surface area, then the previous experimental constant of $10^{-17} - 10^{-16}$ cm⁴s⁻¹ for a single crystal film needs to be modified if it is to be applied to a porous nanoparticle film.⁴ If we replace the two dimensional *J(E)* with a three dimensional current density, then we are able to equate the previously reported values with our experimentally determined values. Figure S5 shows the relationship between the projected surface area A_{proj} and the actual TiO₂ surface area A_{surf} . If we consider the nanoparticles to be packed as shown in Figure S5, which provides a good balance between densely packed regions and voids in the film, then the actual surface area is calculated as

$$A_{surf} = \frac{\pi t}{d} A_{proj}$$
 (S1)

where *t* is the film thickness and *d* is the nanoparticle diameter. In the case of our work, 30nm diameter particles were used to produce a film thickness of 1.7μ m, and the Co³⁺ concentration was 4.2 x 10^{19} cm⁻³. This information was used to derive a charge transfer constant appropriate our investigation, which is presented in our results section.



Figure S5. Relationship between the projected area of the film A_{proj} and the actual area of the nanoparticle surface A_{surf} . The moderate packing of the film allows for an approximate balance between dense packed regions and voids in an actual TiO₂ film.

References

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