Electron transport in nanostructured TiO_2 films

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There is currently a great deal of interest in the properties of electron transport in nanostructured materials permeated with a liquid phase. Here we report on the electronic conductivity, σ, of nanostructured TiO_2 in aqueous solution. We combined different measurement techniques in order to cover a wide scan of the Fermi level through the bandgap. We discuss the interpretation of the results in terms of the electron transport mechanisms.

When the nanoporous TiO_2 is biased positively the Fermi level lies very far from the conduction band; hence the carrier concentration is low and the conductivity is very low. In this region we used the electrochemical impedance spectroscopy (EIS) in the normal configuration, with the potential in the nanoporous electrode being modulated against the reference in solution.[1] As the electrode potential is displaced in the negative direction, the Fermi level moves forward in the direction of the conduction band edge. Then the conductivity increases exponentially and the resistance in the direction normal to the substrate becomes very low, thence it cannot be determined by EIS. In this case it is much better to determine *in situ* the conductivity in the twin electrode configuration, in which two halves of the film electrode are separated by a non-conducting gap in the substrate.[2, 3] In this second case, the conductivity across the gap can be measured only if σ is large. So both techniques are perfectly complementary.

The results of our measurements are shown in Fig. 1. The match of results of the two techniques is excellent. The overall behaviour of the conductivity shows two different domains separated by the crossover at -0.5 V vs. Ag/AgCl. This potential corresponds to the edge of the conduction band of nanocrystalline anatase TiO_2 at *pH* 2.[4] In the positive potential side, the variation of σ can be understood in terms of the progressive displacement of the Fermi level towards the conduction band (band edge pinning). Here the variation of σ is close to $\exp(-eV/k_BT)$, where e/k_BT is the thermal voltage, in other words the variation is near to 60 mV/decade. On the other hand, at potentials more negative than -0.5 V vs. Ag/AgCl a saturation of the conductivity is observed, which is very probably due to a state of pinning of the Fermi level when it is gets close to the edge of the conduction band.

In order to understand the meaning of these results it is also necessary to consider the increase of electron carriers as a function of the bias, which is related to the film capacitance. This can be determined either by EIS or linear sweep voltammetry, and our results[1, 5] in agreement with many others indicate that nanostructured TiO_2 posseses an exponential distribution of band gap states which is the dominant destiny for injected electrons.

We will consider the explanation of the conductivity features in terms of different models. (a) Increasing electron concentration with a constant diffusivity (free electrons model). (b) A standard multiple trapping scheme, where transport of electrons occurs through a band of extended states and is slowed down by the trapping events, which become less probable when the Fermi level is higher. (c) A new model based on hopping conductivity theory in order to explain the electron transport in nanostructured TiO_2.

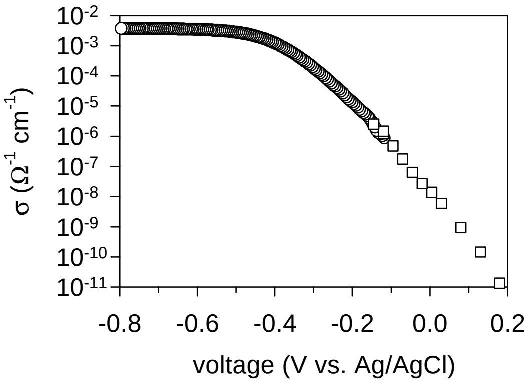

Fig. 1. Electronic conductivity in nanostructured TiO_2 electrodes in solution at *pH* 2 as a function of the bias potential with respect to Ag/AgCl. The square points were determined by electrochemical impedance spectroscopy with the working electrode operating against solution in the normal configuration as reported previously.[1] The circle points were determined in a twin electrode coplanar configuration by simultaneously biasing the two working electrodes with respect to a common reference and measuring the current flowing between them.

References

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