An equivalent circuit approach to the modelling of the dynamics of dye sensitized solar cells

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Abstract

A model that can be used to interpret the response of a dye-sensitized photo electrode to intensity-modulated light (intensity modulated voltage spectroscopy, IMVS and intensity modulated photo-current spectroscopy, IMPS) is presented. The model is based on an equivalent circuit approach involving a transmission line with both an electrical and an ionic branch. An analytical expression including a term from the passive electrochemical impedance of the network, and a term accounting for the photo generation in the electrode is found. From this model IMVS and IMPS responses as well as iV curves can be calculated and used to optimize the photo electrode with respect to thickness and density. The result is mathematically equivalent to the usual approach for IMVS and IMPS modelling based on diffusion equations describing the transport of electrons in the semiconductor and on charge accumulation in traps, although these assumptions are not included in the transmission line model. The diffusion-like behaviour shows up as a consequence of the topology of the coupling between transport processes rather than as an inherent property of the electron transport itself. In this model electron trapping occurs because of electrostatic interactions between electrons in the semiconductor and ions in the electrolyte.
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Keywords: Dye-sensitized solar cells; DSSC; IMVS; IMPS; Modelling

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1. Introduction

Devices for electrochemical energy conversion rely on coupled transport of electronic and ionic species. The rate-determining step is often the shift from electronic conduction to ionic conduction at an electrode–electrolyte interface. One way to increase the efficiency of such cells is to increase the interfacial area, e.g. by making the electrodes porous—relying on an interpenetrating network of electrode phase and electrolyte phase to provide a large area interface. Optimizing such electrodes with respect to power and energy density requires careful balancing of the activation loss at the interface with the transport losses in the electrode and electrolyte phases. Generally this is a classical optimization problem where each of the losses may be reduced at the expense of the others. This optimization can be carried out either through trial and error based on the experience collected through more than a century of battery and fuel cell engineering, or with the aid of mathematical or numerical models. Modelling not only presents a short-cut to device optimization, it also allows one to interpret the outcome of experiments as it may help to de-convolute the response of a complex structure like a porous electrode into separate contributions from properties of individual materials and geometrical parameters.

Mathematical models of porous electrodes are often based on an effective medium approach [1] where contributions from the individual electrode and electrolyte elements are averaged over space so all bulk and interfacial properties are present in each volume element in a proportion dependent on volume fractions and surface area. In this way the dependencies on the exact shapes of the pores and particles are lifted, and the dynamics of the system can be treated in a consistent, general manner. The topology of the electrode may be included in such models by introduction of tortuosity factors.

Dye-sensitized (DSSC), or photo electrochemical (PEC) solar cells [2] have over the last decade attracted a large interest because they represent an interesting alternative to solid-state junction devices, and because of their potential for low-cost production. DSSCs consist of a porous semiconductor photo electrode sensitized with a dye chemisorbed onto its large internal surface, a redox electrolyte, and a counter electrode activated with a catalyst layer. The working principle of a DSSC is sketched on Fig. 1. A photon is exciting the dye absorbed on the anatase surface. The transfer of electrons from dye to the conduction band, CB, of the anatase nano-particles is fast—in the femtosecond region [3]. The oxidized dye is immediately reduced to its initial state by iodide in the electrolyte. In this way the photo-generated charge carriers are efficiently separated into the anatase phase and the electrolyte phase. This will substantially reduce the chances of charge recombination. Charge recombination is, however, still possible through the reduction of tri-iodide with electrons from the CB or from electrons trapped in surface states of anatase. The tri-iodide generated at the photo electrode eventually diffuses to the counter electrode where it is reduced to iodide and becomes available for further charge transport to the photo electrode.

The DSSC cell is a good example of an electrochemical energy conversion device with complex dynamics. Modelling of the porous photo electrode is more involved