Electrochemical methods in dye-sensitized solar cell research

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The development of dye-sensitized and perovskite solar cells (DSSCs and PSCs) is based on the synergy of several areas of pure and applied chemistry, notably synthetic chemistry, materials science, photochemistry-photophysics, and electrochemistry. In the case of DSSCs, electrochemical methods have been used for the characterization of either entire devices or their components and can provide important feedback to the researchers developing and optimizing DSSC materials. Some important examples from the authors’ research obtained over the past 30 years will be cited in this presentation, which will be focused on the electrochemical characterization of DSSC components and the preparation of some of them by electrochemical deposition. At first, the electrochemical reversibility and redox potential of the dye should be investigated, with the dye either in the dissolved state or adsorbed at the electrode, the electrochemical reactivity in the latter case being based on lateral electron transfer (electron hopping) between dye molecules. The redox potential obtained in the latter case is more relevant for the DSSC device, and it can be substantially different from that of the dissolved dye. The semiconductor properties of the mesoporous dye substrate material itself can be characterized by cyclic voltammetry in order to ascertain that the material itself is essentially electrochemically inert at electrode potentials approaching the redox potential of the proposed mediator.

Other studies concerning the photoelectrode, involve the investigation of the effectiveness of the thin semiconductor blocking layer or underlayer (UL) interposed between the mesoporous layer and the transparent conducting oxide (TCO)-coated glass support, which is effective toward suppressing the reactivity of TCO electrons toward the redox mediator. Anodic electrochemical deposition can also be used in order to generate a variant of UL, by anodic electrooxidation of TiCl₃ in an acidic solution. Recently, this type of underlayer was used in PSCs is place of the spray pyrolysis underlayer, with the solar-to-energy efficiency of the resulting devices reaching 21%. As regards redox mediators in liquid DSSC electrolytes, the redox potential and the diffusion coefficient are determined by cyclic voltammetry at stationary electrodes and rotating disk voltammetry at a microelectrode respectively, in the presence of inert supporting electrolyte. Additionally, the effective diffusion coefficient (including migration effects) of the mediator in the electrolytes used in the DSSC device can be determined by linear scan or cyclic voltammetry either at microelectrodes or at symmetrical thin-layer solar cells (TLSCs) with two identical conductive electrodes. Cyclic voltammetry is also used in determining the redox properties of hole conductors used in PSCs. The electrocatalytic properties of the counter electrode (CE) can be investigated either by cyclic voltammetry as well as by impedance spectroscopy, in the latter case at TLSCs with two identical electrodes composed of the same electrocatalyst. Moreover, some types of CEs can be prepared by electrodeposition, for example thin layers of a noble metal or a conducting polymer on a metal or TCO substrate. Finally, electrodeposition can be used in order to generate in-situ, into to the porous of the mesoscopic oxide, a conducting polymer hole conductor, e.g. PEDOT, thereby ensuring intimate contact between the dye and the hole conductor.