

## JUNCTION ADMITTANCE OF DYE SENSITIZED NANOPOROUS TiO<sub>2</sub> SOLAR CELLS

G. Kron<sup>a</sup>, G. Nelles<sup>b</sup>, T. Miteva<sup>b</sup>, A. Yasuda<sup>b</sup>,  
J. H. Werner<sup>a</sup>, U. Rau<sup>a</sup>

<sup>a</sup>Institute of Physical Electronics, University of Stuttgart,  
Stuttgart, Germany

<sup>b</sup>Sony International (Europe) GmbH, MSL, Stuttgart,  
Germany

Dye sensitized solar cells (DSSC) are a promising technological alternative to conventional pn-junction solar cells, and therefore attract considerable scientific interest. Different attempts have been made to replace the liquid electrolyte by a solid state hole conducting organic or inorganic medium.

This contribution compares electrical properties of three different types of DSSCs. First, we use the standard electrolyte device with an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple solved in acetonitrile. Second, we investigate a solid state device with the organic hole conductor MEO-Spiro-TAD. The third type of device under examination is a DSSC that works with a polymer gel electrolyte.

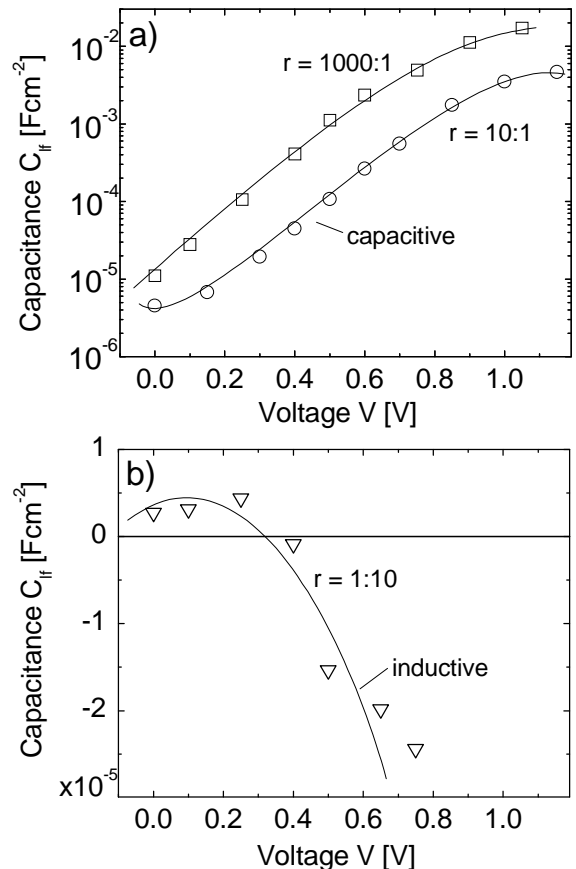
This contribution investigates those three types of solar cells by admittance spectroscopy. The low-frequency conductance  $G_{lf}$  and capacitance  $C_{lf}$  of the liquid electrolyte DSSC increase exponentially upon increasing bias voltage  $V$  (figure 1a). We attribute this exponential increase to a diffusion admittance resulting from injection and subsequent diffusion of electrons in the conduction band of the TiO<sub>2</sub>. From the two quantities,  $C_{lf}$  and  $G_{lf}$ , we calculate an  $RC$  time constant  $\tau_{CG} = C_{lf}/G_{lf}$  which in case of conventional pn-junction solar cells would give the lifetime of electrons. The values for liquid electrolyte cells are in the range of  $\tau_{CG} \approx 100$  ms at a voltage  $V$  close to the open circuit voltage  $V_{oc} \approx 0.75$  V. The time constant  $\tau_{CG}$  depends on the applied bias voltage and the level of illumination.

The low-frequency capacitance  $C_{lf}$  of the solid state DSSC decreases with increasing forward voltage and for  $V > 0.3$  V becomes even negative. This inductive behavior originates from electrons injected from the SnO<sub>2</sub> front electrode into the TiO<sub>2</sub>. These electrons modulate the number of holes in the hole conductor and thus reduce the resistance within the pores. The time delay between electron injection and the modulation of the hole concentration leads to the observed inductive behavior. The occurrence of negative capacitance values does not allow us to calculate an  $RC$  time constant comparable to the electrolyte device.

The behavior of the gel electrolyte cell appears to be right between the other two types of DSSC. For voltages  $V < 0.75$  V, we observe the same exponential increase in the capacitance  $C_{lf}$  as in case of the liquid electrolyte cell. Also,  $\tau_{CG}$  is of similar order of magnitude. For voltages  $V > V_{oc}$ , i.e. for high electron injection densities, the gel electrolyte DSSC changes to inductive behavior.

In the liquid electrolyte DSSC, we observe the effect of inductivity if we reduce the concentration of positive charged Li<sup>+</sup> ions. The concentration ratio Li:I<sub>2</sub> is  $r = 10:1$  in the standard electrolyte. Upon changing this ratio to  $r = 1:10$ , we find an inductive behavior for  $V > 0.4$  V as shown in figure 1b. Thus, we are able to control the capacitive behavior of the device by controlling the charge density in the electrolyte. We determine  $\tau_{CG}$  for the liquid electrolyte DSSCs with a Li:I<sub>2</sub> ratio of  $r = 1:10$  and  $r = 1000:1$ . The time constant  $\tau_{CG}$  increases with decreas-

ing I<sub>2</sub> concentration because of the decreasing availability of I<sub>3</sub><sup>-</sup> recombination partners for the electrons. Thus, basically all features of the junction admittance of electrolyte DSSCs are controlled by the ion concentration in the electrolyte.



**Figure 1:** The exponential increase in  $C_{lf}$  for  $r = 10:1$  and  $1000:1$  is due to injection and diffusion of electrons in the TiO<sub>2</sub>. For a ratio  $r = 1:10$  we observe an inductive behavior.