### The Impedance Analysis of Internal Resistances of Dye-Sensitized Solar Cells and Influence of The **Resistances on The Photoelectrochemical** Performances

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# Introduction

The electrochemical impedance spectroscopy (EIS) is a powerful tool for analyzing dye-sensitized solar cells (DSCs). Electron transfer processes with different rates in DSCs can be examined by this method. In addition, EIS is applicable to DSCs not only at open circuit condition but also under a wide range of operating conditions. Some studies on DSCs employing EIS have been reported so far. However, most of the studies do not refer to the relations between the electrochemical performances of DSCs and electrochemical resistances caused by electron transfer processes in DSCs. This study aims to analyze internal resistances in various dye-sensitized solar cells by ac impedance spectroscopy and to investigate relations between internal resistance and performance of the cells.

#### **Experimental**

The preparation method of TiO<sub>2</sub> electrodes employed was a standard tape-cast method. As a counter electrode, a thin Pt layer was deposited on a conductive glass substrate. As the electrolyte solution,  $I^{-}/I_{3}^{-}$  redox couples were employed. A 50 µm thick thermoplastic resin film was sandwiched between the two glass substrates, and then the assembly was heated on a hot plate to tighten the seal. The electrolyte solution was filled between the two glass substrates. Three-electrode cells were assembled by referring to the method by Zaban et al<sup>1</sup>.

Standard measurements for I-V curves and impedance were carried out under 100 mW cm<sup>-2</sup> illumination and applied open circuit voltage as bias. Impedance measurement of cells was recorded over a frequency range of 3  $\times$  10<sup>-2</sup> to 3  $\times$  10<sup>5</sup> Hz with ac amplitude of 10 mV.

#### **Results and discussion**

It is known that the impedance spectrum in Nyquist representation of the DSC consists of 3 or 4 semicircular components caused by charge transfers at electrochemical interfaces. In particular, the arc  $\omega_3$  whose characteristic frequency is around 10 Hz has great relation to the performance of the DSC. This component was reduced as the irradiation light to the DSC became stronger. And then the short circuit currents increased. On the other hand, in the case that the amount of I2 dissolved in electrolyte for DSCs was decreased, the short circuit currents increased though their arcs  $\omega_3$  were larger as shown in Fig. 1. This arc component has been attributed to the electron transfer process at TiO<sub>2</sub>/redox electrolyte <sup>2</sup>, , and its characteristic frequency at open circuit voltage shows the same value as the characteristic frequency obtained from intensity-modulated photovoltage spectroscopy (IMVS)<sup>4</sup>. Therefore, this frequency reveals the electron lifetime  $\tau_n$  of the recombination process at  $TiO_2/redox$  electrolyte. Figure 2 plots  $\tau_n$  and short circuit current as a function of the amount of  $I_2$  in electrolyte. The electron lifetimes of the recombination process were longer as the amount of I<sub>2</sub> was reduced. This result can be explained as follows: when few electron accepters  $I_3^-$  exist at  $TiO_2$ /electrolite interface, the frequency for the recombination is diminished. Nevertheless, short circuit currents at low amounts of I2 did not necessarily increase. Other impedance components seem to affect short circuit current

Impedance measurements using three-electrode system have a potential to give further information on impedance of DSCs. Particularly, since the impedance at Pt counter electrodes are generally negligibly small for comparison with that at TiO<sub>2</sub> electrodes, this method is available for analyzing the impedance at Pt electrodes. We will also present the results from this experiment.

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Fig. 1 (a) I-V curves and (b) Nyquist plots of dyesensitized solar cells under 100mW cm<sup>-2</sup> light irradiation. Different quantities of I2 were dissolved in electrolyte.



Fig. 2 The relations among amounts of I<sub>2</sub> in electrolyte,  $\tau_n$  and short circuit current under various irradiation light intensities,  $\bullet O$ : 100mW cm<sup>-2</sup>,  $\blacksquare \Box$ : 88.9 mW  $cm^{-2}$ ,  $\clubsuit$ : 77.8 mW  $cm^{-2}$ ,  $\blacktriangle$ : 55.6 mW  $cm^{-2}$ .