Photoconductivity Analyzed in the Frequency Domain – An Introductory Case Study of Strontium Titanate

Dino Klotz, WPI International Institute for Carbon Neutral Energy Research (I^2CNER), Kyushu University
dino.klotz@i2cner.kyushu-u.ac.jp

Strontium titanate (STO, $SrTiO_3$) has been used for many applications in solid state electrochemistry and is considered a standard and model material. Its characteristics, and those of its derivatives such as STF ($SrTi_{0.65}Fe_{0.35}O_{3-x}$), have been characterized by many groups on various aspects, such as electronic/ionic conductivity, oxygen exchange kinetics and the impact of doping. Recently, the interaction of light with STO/STF has been of increased interest. A persistent photoconductivity has been observed [1] and enhanced oxygen exchange kinetics has been detected, opening up new fields of application, such as a light-driven fuel cell [2].

The reasons behind these effects remain subject to discussion or even speculation as the relation to the relatively large bandgap and the photoresponse at long wavelengths remains unclear. What makes the analysis of these effects difficult is the interplay of many electrochemical and photoelectrochemical processes that contribute to the photoresponse including the electronic and ionic conductivity, the number and nature of charge carriers, charge traps, phonon related effects, and surface reactions. With electrochemical impedance spectroscopy (EIS), one can distinguish diverse processes on the basis of their time constants and how they evolve as a function of operating conditions, such as temperature, atmosphere (leading to stoichiometry changes) and illumination. However, the impact of light can only be characterized implicitly as a change in other processes that also prevail in the dark.

Intensity modulated photocurrent/-voltage spectroscopy (IMPS/IMVS) have been shown to reveal valuable information about charge carrier dynamics for photoelectrodes and photovoltaic cells [3]. To the best of our knowledge, these techniques have never been applied to devices or materials that are not photoactive, or in other words, that do not show a photovoltage, such as a symmetrical model cells based on STO or STF. However, with the small signal light perturbation that is the key element of IMPS and IMVS, we can trigger the light effect directly and analyze the system response by its current and voltage signals.

In this contribution, we will begin with a brief introduction into IMPS and IMVS and show how these techniques can be applied to model electrodes consisting of STO and STF. The results are compared to EIS under different illumination and we will show how to extract the relevant information about the photoresponse. By evaluating the activation energies of the different electrochemical and photoelectrochemical processes, we can attribute those to physical effects and clarify some of the previously unknown processes that lead to anomalies observed in STO/STF under illumination.

The capacity of IMPS and IMVS have been underestimated so far and in this contribution, we will conclude with an outlook for their potential to other fields of application, such as ionic motion in perovskite solar cells that are thought to be responsible for their accelerated degradation under illumination.

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References

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