Unveiling the Working Mechanisms and Limitations of Photoconversion Devices through Modulated Techniques

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In recent decades, the field of photoconversion devices has witnessed remarkable progress. However, promising technologies like perovskite solar cells and photoelectrochemical cells for hydrogen generation still grapple with limitations, particularly in stability and performance, hindering their widespread commercialization. Addressing these challenges necessitates a profound understanding of the internal mechanisms governing the operation of these devices and a systematic identification of their key limitations. In this presentation, I will elucidate the potential of modulated techniques, also known as small perturbation techniques, to unveil these internal mechanisms during the operation of photoconversion devices.

Starting with an exploration of the most widely adopted modulated technique, impedance spectroscopy (IS), I will delve into the intricate relationship between IS and current versus voltage curves. Specifically, I will present the correlation between the observation of negative capacitances in IS responses and the manifestation of inverted hysteresis in cyclic voltammetry.[1] Experimental results for perovskite-based devices will be showcased, highlighting their inductive-like behavior, an essential aspect for memristors.

Despite the considerable power of IS for in-operando device analysis, this technique has its limitations. Consequently, the talk will delve into how these limitations can be effectively addressed by combining IS with two additional modulated techniques: intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS). While the analysis of IMPS and IMVS spectra traditionally focuses on characteristic times, the analysis of an IS spectrum is usually made through an equivalent circuit (EC) model, but the selection of the proper EC can be challenging. A novel procedure for jointly analyzing IS, IMPS, and IMVS responses will be presented.

To underscore the efficacy of this combined analysis, two practical applications will be showcased, a silicon photodiode[2] and an electrochemical hydrogen generation cell with a Zr:$BiVO_4$ photoanode[3]. Our findings demonstrate the possibility of analyzing all three techniques with the same equivalent circuit, selected with enhanced precision. Furthermore, the combined analysis yields more accurate parameters compared to individual analyses, and it allows the acquisition of additional parameters, including the separation efficiency.

References:

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[3] A. O. Alvarez, M. García-Tecedor, L. Montañés, E. Mas-Marzá, S. Giménez, F. Fabregat-Santiago, Sol. RRL 2022, 6, 2200826