Electrochemistry of Oxide Semiconductors (SnO$_2$ TiO$_2$ and ZnO) in Aqueous and Aprotic Media

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While the majority of experimental and theoretical work on semiconductor electrochemistry has been conducted in aqueous electrolyte solutions [1, 2], studies in aprotic media are relatively limited. However, electrochemistry in, e.g., LiTFSI+acetonitrile provides valuable insights for applications in energy storage and conversion, such as Li-batteries and dye-sensitized solar cells [3, 4]. Optimizing of these technologies requires detailed information about the electronic structure near the conduction band minimum (CBM) of an oxide semiconductor [5]. However, the analysis of CBM structure is challenging, sometimes even impossible for fundamental reasons [4-6]. By investigating a representative array of materials, ranging from macroscopic single crystals in different face orientations to polycrystalline and quasi-amorphous thin films on various substrates, we explored their electrochemical behavior in both aqueous and acetonitrile electrolyte solutions. This yielded quite self-consistent information, also highlighting some issues with a more general impact [4]. Representative examples of these challenges include: (i) Determination of flatband potentials and donor concentrations by Mott-Schottky analysis, particularly for nanotextured materials. There is a significant spread of flatband potentials for TiO$_2$, SnO$_2$, and ZnO, and overestimated concentrations of majority charge carriers, which could even incorrectly predict degenerated semiconductors [2]; (ii) Calculation of work functions and band edges by DFT, ignoring the effects of sample environment and/or defects in real crystals [4, 7]; (iii) Measurement of work functions and band edges by a single experimental technique only (e.g., by photoelectron spectroscopy, Kelvin probe, or electrochemistry), disregarding the inherently poor reproducibility of values from each individual technique [4, 6]; (iv) Transposition of these problematic data, both theoretical and experimental, into discussions of water splitting, solar fuel generation, solar cells, and Li-ion batteries [4]; (v) Application of the Gärtner-Butler model for carrier dynamics in a semiconductor photoanode, disregarding the gradient of electrochemical potentials as the driving force for e$^-$/h$^+$ separation [4, 8].

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