

ABSTRACT

Meeting the demand of a global energy thirst, while avoiding environmental damages, poses a major scientific and societal challenge for our future. Hydrocarbons will continue to play the major role on the next few decades, but their costs are doomed to increase while their availability decrease. Besides fossil fuels, there are many other energy sources like nuclear fission, wind, biomass and geothermal, but in the long term the most appealing and widely distributed is solar, providing ~10000 times the energy currently consumed worldwide. Because of its unmatched resource potential, solar energy utilization has been the subject of intense research, development, and deployment efforts that have accelerated during the past decade. Efforts have been focused on the development of photovoltaics (PVs) for production of solar electricity, on conversion of solar energy into heat, and on development of artificial systems that directly produce fuels from sunlight. Chemistry has played a fundamental role in the design of materials and molecular systems for solar energy conversion. On the other hand, the radiation that reaches the earth, despite is extensively distributed, presents a low intensity and its availability depends on geography, day and night alternation, and cloud cover. As a consequence, solar has to be coupled with efficient storage systems such as rechargeable batteries, which are able to store and release electric power when required. Scope of this PhD thesis was both the preparation of photoelectroactive substrates, based on wide band-gap semiconductor electrodes, functionalized with molecular sensitizers to convert solar energy into electricity, namely dye sensitized solar cells (DSSCs) and into fuels, namely dye sensitized photoelectrochemical cells (DSPECs), and the study of a storage system based on electrolytes containing one or more electroactive species, namely Redox Flow Batteries (RFBs). After discussing some general notions about renewable sources (**Chapter 1**), about the basic features of DSSCs, DSPECs (**Chapter 2**), and RFBs (**Chapter 3**) the study of the systems employed during this PhD is described.

The focus of **Chapter 4** and **Chapter 5** is the study of new redox mediators for DSSCs as an alternative to the well-known Co(II)/Co(III) and iodide/triiodide couples. In **Chapter 4** the photoelectrochemical properties and stability of dye sensitized solar cells containing Mn(β -diketonato)₃ complexes as redox mediators have been evaluated. At room temperature, the complexes undergo ligand exchange with 4-*tert*-butyl-pyridine (TBP), an additive commonly used in solar devices. An increased device stability was achieved by using a ruthenium based dye and passivating the photoanode with short chain siloxanes. In addition, a new Manganese complex with an encapsulating ligand, which is stable in TBP presence, was synthesized and tested. While, in **Chapter 5**, was explored the possibility to couple β -substituted Zn²⁺ porphyrins with copper redox

mediators. Furthermore, a new copper electrolyte which reaches performance able to overcome the ones reached with iodide/triiodide and Co(II)/(III) reference couples, was studied.

In **Chapter 6** the electrochemical properties of a series of Iron and Cobalt complexes, based on chelate ligands, were explored with the aim of finding promising candidates for application in high voltage redox flow batteries. The reported compounds were selected by considering the stability of the electrochemical response of the Fe(III)/(II) and Co(II)/(I) couples on carbon based electrodes and their solubility in a mixture of ethylene and propylene carbonates (EC:PC) chosen as low volatility and electrochemically stable solvents. The most promising compounds, which lead to limiting current of the order of 30 mA/cm² in thin layer cell, were also preliminarily tested in a lab. scale flow cell equipped with a Nafion membrane, where a good stability and reversibility in open circuit potential (≈ 1.9 V) and *ca.* 90 % coulombic efficiency were recorded.

In **Chapter 7** is reported the possibility to combine wide band gap semiconductors like SnO₂ and Sb-doped SnO₂ (ATO) with perylene (PDI)-based aggregates to find an efficient nanostructured photoanode for photoelectrochemical solar fuel generation. A detailed analysis of semiconductor properties was carried out in order to understand interfacial energetics, charge separation and charge transfer dynamics. An interesting behaviour associated to Sb-doped SnO₂ was found. Indeed, due to Sb doping, ATO showed a significant density of deep intra band states, which are absent in pure SnO₂. The presence of these states, whose occupancy varies with the applied potential, plays a substantial role in tuning the efficiency of photoinduced charge separation and collection of ATO-PDI system. The role of surface states seems to be much less pronounced in PDI/SnO₂ electrodes but still an influence of the pH on the charge injection and collection efficiency of SnO₂-PDI photoanodes was observed through an evaluation of the incident photon-to-current conversion. This suggests that in such systems the energy of the semiconductor states can be tuned independently from the molecular levels, allowing to improve the photoanode quantum yield in the case of poorly reducing excited states.

