Chapter 8

Conclusions and Future Scope

In conclusion, we have studied different devices utilizing PbO$_x$/electrolyte and PbO$_x$/metal interface. In this study, a new technique for anodization of lead metal was explored. It was found that the potential pulse technique results into the generation of nanowall assemblies of nonstoichiometric PbO$_x$ all over the active area for anodization. With aqueous electrolyte, we have recorded high photocurrent density of 4.03 mA/cm$^2$ without doping this nonstoichiometric semiconductor. For the first time we have made efforts to understand a typical shape of the photocurrent characteristic of PbO$_x$ electrode by using A. C. techniques. The charge transfer mechanism of PEC cell configured as PbO$_x$ (0.25 cm$^2$)|Fe(CN)$_6^{4-/3-}$ electrolyte (9.2 pH)|Platinum (2 cm$^2$) was studied in detail by impedance, conductance and capacitance measurements. The equivalent circuit analysis was utilized to understand the nature of the photoresponse. It was also found that the dominant charge transfer mechanism of PEC cell based on PbO$_x$ photoanode is hopping via trap states. The activation energies of traps were found to be only 0.2 and 0.8 meV and hence the traps actively participate into conduction even under dark condition at room temperature. To overcome the stability issues, we have tried two different ways: 1) To use the ionic liquid as an active electrolyte 2) To fabricate solid state Schottky junction solar cells using appropriate metal. During the first approach, it was found that blank ionic liquids are redox active medium, which can be directly used in replacement of any other conventional electrolytes.
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The photocurrent densities of 1.78, 1.74 and 2.47 mA/cm² were obtained for PbO₂ electrodes configured using blank BMIIm Cl, BMIIm PF₆ and BMIIm Tf₂N, respectively. The inherent redox active nature of ionic liquids was explained on the basis of the concept of ionicity and ion-pairing mechanism. The PEC cells made by using blank ionic liquids were found to be inferior in performance as power generating device. The lower V⁺ was attributed to the specific adsorption of ions, which was experimentally seen from low frequency capacitance-voltage characteristics. Though, the frequency degeneracy makes the Capacitance-Voltage measurements difficult to perform in ionic liquid medium, we have showed a way in which selective frequency measurements can give accurate results. We have also made efforts to accurately determine the redox potential (E⁺) of the ionic liquids under investigation. The redox potentials of blank ionic liquids were found to be 0.30, 0.29 and 0.78 V (vs. NHE) for BMIIm Cl, BMIIm PF₆ and BMIIm Tf₂N, respectively. These values were recalculated by utilizing the interface with other semiconductor (CdS). The charge transfer properties of blank ionic liquids were studied by photocurrent and impedance measurements. It was found that the redox processes via ion pairs of ionic liquid are partially reversible and the ion pairs being consumed during the charge transfer process. We extended the impedance study by adding another redox couple (Fe(CN)₆⁻¹/³) in BMIIm Cl to see the performance of redox active ionic liquid as medium. The effect of external redox couple on the performance of ionic liquid PEC cell is explained by assuming inter redox couple charge transfer. It was also found that addition of one more redox couple (Fe(CN)₆⁻¹/³⁻³) in IL improves the dark current characteristic of the PEC cell, resulting into a wider photoelectrochemical window (>3 V). The participation of the ionic species of the ionic liquid in ion pair formation and involvement of the ion pairs in the charge transfer process resulted into the fluidization of ionic liquid. This phenomenon was experimentally supported by taking photoreponse after 2 minutes of interval. The solid state Schottky junction solar cell of PbO₂ were fabricated by making interface with Au-Pd alloy. The PbO₂ films prepared via two different techniques were used as an active layer of such solar cells. It was found that the optimized thickness of 1 nm of Au-Pd alloy is required for potentiodynamic PbO₂ film,
whereas the potential pulse PbO$_x$ film required 10 nm thick alloy for its optimum performance. The electrical parameters of these devices were calculated by using dark J-V characteristics. With the potential pulsed PbO$_x$/Au-Pd cell, we achieved highest $J_{sc}$ of 2.04 mA/cm$^2$ with $V_{oc}$ of 707 mV giving an overall efficiency of 0.384%. However, cells prepared using potentiodynamic technique resulted into the efficiency of 0.204% with high fill factor of 49%, $J_{sc}$ of 0.574 mA/cm$^2$ and $V_{oc}$ 727 mV. The higher ideality factor of the potentiodynamically prepared cells is attributed to the existence of trap states. The activation energies of trap states were found to be 0.124 and 0.01 eV for the cells made using PbO$_x$ prepared by potentiodynamic and potential pulse techniques, respectively. A detailed impedance study revealed the reasons for superior performance of potential pulse cells. The lower contact and series resistance increased the $J_{sc}$ of potential pulse cells, whereas higher bulk resistance increased the $V_{oc}$ in the case of cells prepared by potentiodynamic technique.

The PbO$_x$ films prepared in this study contained both the phases alpha and beta PbO, however, for future work it would be much beneficial to have PbO$_x$ films with only alpha PbO phase. For doing so, one can opt for combination of potentiodynamic and pulse techniques by appropriately choosing the potential values. Further we have speculated the redox processes of blank ionic liquid on the basis of experimental observations. This study can be extended by analyzing the interfaces using appropriate spectroscopic or optical techniques. The role of anion and cation in partial charge transfer can also be understood by thoroughly investigating the interface properties. In addition, there exist a number of ionic liquids which can be explored to enhance the performance of PEC cells as power generating devices. We believe that the properties of ionic liquids are still under explored and a rigorous research is required to set a database of their magical properties. At the end, an early stage investigation on PbO$_x$ solid state devices invoke the possibility of this material to be used in photovoltaic devices. If proper optimizations are achieved then the low cost solar cells can be fabricated by using PbO$_x$ films which might find suitable application in portable charging devices. We also believe that the issue on recycling or reuse lead acid batteries can be overcome by adoption of
such solar cells.