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Abstract of Plenary Talk – I

The Role of "Mixed Cations" in Electrolytes of Dye Sensitized Solar Cells

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Dye sensitized solar cells (DSSCs) based on nanostructured titanium dioxide (TiO_2), offer a low cost alternative to conventional silicon and thin film solar core stable cells can be fabricated by replacing the liquid electrolyte by quasi-solid (gel) or solid electrolytes at the expense of their efficiency. The efficiency enhancement in these solar cells has therefore become an important research problem. In solar cells using iodide-tri-iodide as the redox couple, the iodide salt, particularly the cations, play a vital role in determining the short circuit current density (J_{sc}), open circuit voltage and hence the efficiency. Based on independent work on single cation iodide salts by several research groups, it is generally established that, small cations like K^+ and Li^+ can get easily adsorbed by the TiO_2 in the photoanode causing a positive shift in the conduction band of TiO_2 leading to an increase in the J_{sc} while at the same time decreasing the open circuit voltage (V_{oc}) of the cell. The J_{sc} increase is due to the increase in electron injection rate with increase in cation charge density. This positive shift caused by the intercalation of cations varies according to the type and the size of the cation used and the shift is generally higher for small size cations. On the other hand, the adsorption of bulky cations, such as Pr_4N^+ in tetrapropyl ammonium iodide (Pr_4NI), causes only a smaller positive shift in the TiO_2 conduction band favouring the open circuit voltage (V_{oc}).

The beneficial effect of both these mechanisms, the increase in J_{sc} due to smaller cations and the increase in V_{oc} due to bulky cations, can be optimized and harnessed by having a binary mixture of two iodide salts, one with a small cation and the other with a bulky cation. Examples for such systems are: LiI+Pr_4NI, KI+ Hex_4NI, LiI + CsI. These binary iodide salts have been incorporated in several different polymer hosts, such as polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), poly(vinylidenefluoride (PVdF) and polyethylene oxide (PEO) do demonstrate this effect. This "*mixed cation effect*" reported by us several years ago can enhance the solar cell efficiencies by about 20-30% due to the synergetic effect of optimizing the J_{sc} and V_{oc} values. From these studies, it was also established that the variation of the power conversion efficiency with the concentration ratio of the two iodide salts follows the same trend as the short circuit current density (J_{sc}) and goes through a maximum at a particular salt concentration ratio. The observed efficiency enhancement has been explained on the basis of the electrode effects as well as electrolyte effects where the cations play a dominant role.