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Impact of Electrolytes Based on Different Solvents on the Long Term Stability of Dye Sensitized Solar Cells

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ABSTRACT

The present article demonstrates the effect of different solvents used in the preparation of electrolyte on the photoelectrochemical characteristics of dye sensitized solar cells (DSSCs) aged under heat (60 °C) and illumination for 60 days. The study has been carried out with four different solvents: 3-methoxypropionitrile (MPN), N-methyl-2-pyrrolidone (NMP), propylene carbonate (PC) and γ-butyrolactone (GBL) which differ in terms of donor number, viscosity and dielectric constant. For DSSCs with electrolytes based on MPN, PC and GBL as solvents, performance decreases with time. In contrast, for DSSC with NMP as solvent in electrolyte, increase in J_{SC} and hence, efficiency up to 15 days has been observed followed by a gradual decrease, but remaining above its initial value after 60 days. However, V_{OC} of such cell decreases with time. There are two possible causes for the above observations. Desorption of NMP molecules from titania surface occurred with aging. Secondly, zinc ions leached into the electrolyte following reaction of NMP with sealant were adsorbed on titania surface. The causes behind aging behavior of cells prepared with different solvent based electrolytes have been analyzed using electrochemical impedance analysis of DSSCs, energy-dispersive X-ray spectroscopy (EDS) of photoanodes and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of electrolyte containing sealant sample which had also undergone aging under similar condition.

1. Introduction

Dye sensitized solar cells (DSSCs) are known among the different class of photovoltaics as low cost solar cells. Along with that, remarkable efficiency of 12–13% [1,2] in such kind of cells at lab scale project it as a potential alternative to thin film solar cells. The bottleneck of this technology is the achievement of long term stability which would make such cells feasible for outdoor operation. Although efficiency of 10% [3] has been achieved in solid state dye sensitized solar cell, higher efficiency cells are based on liquid electrolytes. DSSCs fabricated with quasi solid electrolytes have shown enhanced stability as compared to liquid electrolytes based cells without compromising in performance [4–6]. Typically, a DSSC constitutes of photoanode, counter electrode and liquid electrolyte containing a redox couple. Each component is responsible for the long term stability of DSSC. Photoanode consist of a dye loaded titania film. It is well known in literature that dye molecules are unstable for long term even though a life time of 20 years is desired. Such molecules react with water from electrolyte or intruded from environment due to improper sealing and also with electrolyte components and undergo chemical change or desorb from the titania surface leading to poor cell stability [7]. In case of titania, DSSC containing titania film fabricated by template approach resulted in higher stability as compared to DSSC fabricated with titania nanoparticles based electrode [8]. Enhanced crystallite connectivity in the former resulted in efficient electron transport and low charge transfer resistance which led to higher stability of cell. Titania film is also likely to undergo changes and crack density of film increases upon aging [9]. Platinum is the most widely used and efficient catalyst for triiodide reduction at counter electrode. The use of iodide/triiodide redox couple along with platinum leads to dissolution of platinum from counter electrode leading to poor triiodide reduction and hence, cell performance decreases over time. It has been observed that such dissolution also occurs at ambient condition [10] and presence of water promotes dissolution of platinum [11].

Several studies have also been carried out in order to observe the effect of electrolyte on cell stability. As commonly known, constituents of liquid electrolyte are redox couple, solvent and

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additives. Redox couple contains various counter ions which affect the performance of dye sensitized solar cell. Such ions get adsorbed on surface of photoanode with effectiveness of adsorption depending on their size. Study on different cations affecting degradation characteristics and long term stability was carried out by Nakade et al. [12]. Decrease in performance over 60 h for cells using lithium ions and tetrabutylammonium ions has been observed. Such decrease was attributed to decrease in electron life time and diffusion length in TiO_2 photoanode. By introduction of tert-butylpyridine to lithium ion based electrolyte, stability of cells improved by co-ordination of both which reduced the adsorption of lithium ion on titania. For tetraalkylammonium cations degradation reaction was proposed which would form basic compounds leading to dye desorption. Imidazolium ion was found to be suitable in their study [12] achieving good stability and unchanged electron lifetime which was attributed to its larger size and flat structure as compared to others. Wyss et al. have examined the effect of different cation structures on long term stability of DSSCs [13]. Iodide salts of 1,3-dimethylimidazolium, 1,2-dimethyl-3-propylimidazolium, 1-ethyl-1-methylpyrrolidinium, tetrabutylammonium and 1-propylpyridinium cations were evaluated. Stability testing for 1000 h was performed at 60 °C under illumination and more than 92% of initial efficiency was retained for all the cells. There are few articles on effect of electrolyte components on cell stability. So, the present study is focused on the effect of different solvents on the long term stability of DSSCs. It is well known that with variation in physical properties like viscosity, dielectric constant and donor number the performance of DSSC changes [14–16]. Hence different solvents in electrolyte may alter the long term stability of DSSC.

Table 1
Physical property of different solvents used in the study [15,17].

Solvent	Viscosity(cp)	Donor Number	Dielectric Constant
MPN	1.1	16.1	36.0
NMP	1.6	27.3	32.2
PC	2.5	15.1	65.0
GBL	1.7	18.0	42.0

2. Experimental

The following solvents were chosen based on their different physical properties like donor number, viscosity and dielectric constant for preparation of electrolytes: 3-methoxypropionitrile [MPN] (≥98% Aldrich) N-methyl-2-pyrrolidone [NMP] (Extrapure, SRL), propylene carbonate [PC] (Puriss, Spectrochem) and γ-butyrolactone [GBL] (Extrapure, SRL). For preparation of the electrolytes, 1-methyl-3-propylimidazolium iodide [MPII] (≥98% Aldrich) and iodine (LR, Thomas Baker) were used along with each solvent. Platinum nanoparticles for preparation of dip coated counter electrodes were synthesized using hexachloroplatinic acid hexahydrate (Puriss, Spectrochem), polyvinylpyrrolidone [PVP] K30 (Puriss, Spectrochem) and 1-propanol (Synthesis grade, Merck). First 1.44 g of PVP was dissolved in 60 ml of 1-propanol by stirring and then 6 ml of 6 mM platinum precursor solution in distilled water was added to it. The solution was stirred for 15 minutes and then refluxed at 110 °C for 1 h. Colour of the solution changed to black indicating formation of platinum nanoparticles.

Fluorine-doped tin oxide (FTO) glass substrates (TEC7, sheet resistance 8-9 Ω □$^{-1}$, Pilkington), TiO_2 nanopowder (P25, Degussa), polyethylene glycol (M_w = 600) [PEG 600] (Thomas

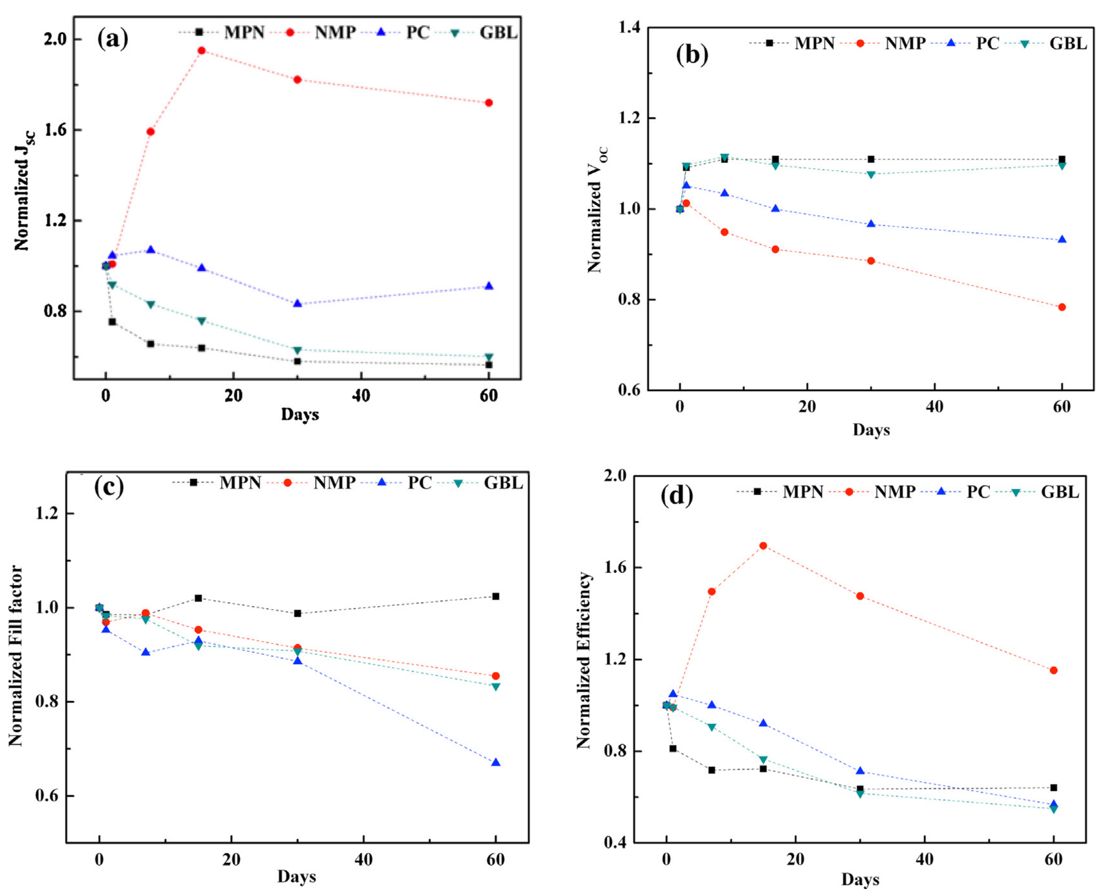

Fig. 1. Variation of photovoltaic parameters of DSSCs fabricated with different solvents upon aging (a) J_{SC}, (b) V_{OC}, (c) fill factor and (d) efficiency.