



Preparation of polyvinylpyrrolidone-based polymer electrolytes and their application by in-situ gelation in dye-sensitized solar cells

D.A. Chalkias^{a,*}, D.I. Giannopoulos^a, E. Kollia^a, A. Petala^b, V. Kostopoulos^a, G.C. Papanicolaou^{a,**}

^a Department of Mechanical Engineering & Aeronautics, University of Patras, 26500 Patras, Greece

^b Department of Chemical Engineering, University of Patras, 26500 Patras, Greece



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ABSTRACT

Polyvinylpyrrolidone (PVP), as a nitrogen-containing heterocyclic polymer, is a promising candidate for preparation of high performance iodide-based polymer electrolytes for dye-sensitized solar cells (DSSCs). In the present investigation, PVP electrolytes composed of different wt% loadings of potassium iodide and iodine were prepared, thoroughly characterized, and applied to DSSCs. The TiO₂ electrode of the solid state DSSCs was optimized (film thickness, dye loading, TiCl₄ treatment), to achieve high energy conversion efficiency. Differential scanning calorimetry, Fourier transform infrared spectroscopy, X-ray diffraction, electrochemical impedance spectroscopy, linear sweep voltammetry, and ultraviolet–visible spectroscopy were used to characterize the PVP electrolytes. One-diode model equivalent circuit analysis was applied to DSSCs characteristic curve, in order to calculate the key electrical circuit elements values, determining solar cells efficiency. The maximum energy conversion efficiency attained by the solid state DSSCs under real test conditions was 3.74%, at about 1000 W/m² irradiation intensity. By in-situ gelation of the PVP electrolytes onto TiO₂, an optimal electrode film thickness on the order of 15 μm was achieved, which is very close to the corresponding value usually attained to liquid state DSSCs. The results are satisfactory compared to DSSCs employing liquid state factory available electrolytes, while simultaneously the PVP electrolytes preparation is simple and of low-cost, having great prospects for further optimization.

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1. Introduction

Since the first report on a high efficient dye-sensitized solar cell (DSSC) by Grätzel in 1991, DSSCs have received considerable attention during the last decades [1,2]. Some of their more attractive features are the low production cost, the satisfactory energy conversion efficiency, and the appealing aesthetics. However, DSSCs wide commercialization is still hampered by a number of issues [3].

In order to make DSSCs widely commercialized, in recent years a lot of research has been carried out to increase their efficiency, reliability and lifetime, as well as to further reduce their manufacturing cost [4,5]. In addition, easily up-scalable at an

industrial level components, processes, and fabrication systems are under investigation, paving the way for pioneer photovoltaic applications [6]. The environmental impact of these devices is also considered to be of great importance. Petroleum-derived, toxic and/or heavy metal-based free biomaterials have been successfully used recently for fabrication of greener DSSCs [7–9].

Amongst the above-mentioned research efforts, particular emphasis is nowadays placed on increasing DSSCs stability, with the aim of developing a solar cell that will operate satisfactorily in the foreseeable environmental conditions for more than 20 years [10]. In view of the above, replacement of liquid state electrolytes with solid state charge transport materials is necessary. Thus, many practical problems, that may arise in the long-term outdoor operation of DSSCs, are prevented. Typical examples are leakage and evaporation of liquids, rupture of the device due to the development of high internal vapor pressure, etc [11].

Several attempts have been made so far to find the ideal replacements of the conventional liquid state electrolytes of DSSCs.

* Corresponding author.

** Corresponding author.

E-mail addresses: chalkias@mech.upatras.gr (D.A. Chalkias), gpapan@mech.upatras.gr (G.C. Papanicolaou).

Nowadays, the greatest worldwide scientific interest concerns preparation and application of thin quasi-solid state polymeric membranes that exhibit ionic conductivity, called polymer electrolytes [12,13]. Polymer electrolytes are usually prepared by swelling a polymer network with a liquid state electrolyte. In the last decade, novel techniques have been applied for polymer electrolytes preparation, in view of production time and costs decrease of the final device, e.g. photo-polymerization and emulsion polymerization [14,15]. At the same time, novel concepts in preparation of quasi-solid state electrolytes appear, leading to promising results for fabrication of high efficient DSSCs with enhanced stability over time [16].

However, in most cases, the high viscosity of polymer electrolytes results in reduced DSSCs energy conversion efficiency, compared to the conventional devices. One of the main problems is the difficulty of polymer penetration into the mesoporous network of the photo-anode [17]. Patterning the geometry of micro-/nanostructures on DSSC working electrode can improve their energy conversion efficiency, by the formation of a better photo-anode/electrolyte electrochemical interface [18]. In-situ gelation of polymers or organic monomers polymerization pre-penetrated into the pores of the DSSCs working electrode is considered the most appropriate technique for fabrication of high performance solid state dye-sensitized solar cells (ssDSSCs) [19–22].

Some polymers that are typically used as solidification agent of liquid state electrolytes are polyethylene oxide, polyacrylonitrile, polyvinylidene fluoride, and methyl polymethacrylate [23–26]. Polyvinylpyrrolidone or polyvidone or povidone (PVP) is also a remarkable conjugated thermoplastic biodegradable polymer that has recently been used to solidify electrolytes for DSSCs application [27–31]. PVP shows high stability under normal environmental conditions, easy processability, good solubility in polar solvents, and excellent wetting properties, while its highly amorphous nature facilitates the movement of ions. In addition, as a nitrogen-containing heterocyclic polymer, PVP can form PVP-iodine complex, a feature that makes it suitable solidification agent of iodide-based liquid state electrolytes. Nitrogen-containing heterocyclic additives in I^-/I_3^- redox electrolytic solutions have been proved, by their application to DSSCs, to lead to an increased open-circuit voltage [32,33].

In the present investigation, PVP electrolytes were prepared and were thermally, structurally, electrically, optically characterized, and subsequently applied by in-situ gelation to DSSCs. The redox couple concentration varied, to achieve high ionic conductivity, combined with low absorbance in visible light, and low back-reaction when the electrolyte is applied to DSSCs. The determination of the optimum working electrode film thickness and dye loading, as well as the $TiCl_4$ treatment of the working electrode, was carried out, in order to further improve the solar cells performance. Finally, ssDSSCs electrical characteristics were compared to the corresponding characteristics of DSSCs employing liquid state factory available electrolytes. In all cases, one-diode model equivalent circuit analysis followed, in order to derive the key electrical circuit elements values, determining solar cells energy conversion efficiency.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone with an average molecular weight of 40,000 (PVP40, Sigma Aldrich), potassium iodide (ACS reagent $\geq 99\%$, Sigma Aldrich), iodine (ACS reagent $\geq 99.8\%$, Sigma Aldrich), methanol (analytical reagent grade, Fisher Chemical), fluorine doped tin oxide glass (TEC 8, 2.2 mm thickness, Dyesol),

titanium dioxide nano-powder (P25, Sigma Aldrich), titanium (IV) chloride (purity $\geq 99\%$, Sigma Aldrich), N719 industry standard dye (Dyesol), high performance liquid state electrolyte (EL-HPE, Dyesol), high stability liquid state electrolyte (EL-HSE, Dyesol), platinum paste (PT1, Dyesol), and low temperature thermoplastic sealant (50 μm thickness, Dyesol) have been used.

2.2. Preparation of polyvinylpyrrolidone-based polymer electrolytes

Polymer electrolytes were prepared by dissolving 500 mg of PVP and different wt% loadings of potassium iodide (KI) and iodine (I_2) in 4 mL of methanol, under continuous stirring in sealed glass vessels, for their complete dissolution. The x wt% KI contents (where $x = 20, 25, 30, 35$ and 40) of PVP:KI mixtures were studied, while the I_2 amount was in all cases fixed at 10 wt% of KI. The electrolytes were stored in the sealed vessels until their in-situ gelation onto the DSSCs photo-anode (Fig. 1).

2.3. Fabrication of dye-sensitized solar cells

A simple chemical technique for preparing a TiO_2 paste from commercially available P25 nanopowder was used as reported elsewhere [34]. The temperature control during the preparation of the TiO_2 paste regulated the viscosity of the paste, for doctor-blading or spin-coating usage. Both techniques were tested for the fabrication of TiO_2 electrodes; single-layered films were fabricated by doctor-blading, while different film thicknesses were obtained by spin-coating, either by configuring the revolutions per minute of the coater or by using more layers. Subsequently, the nanostructured working electrodes were sintered at $500^\circ C$ for 90 min, leading to uniform, mesoporous films, without cracking and peeling-off from the fluorine doped tin oxide (FTO) glass substrates. The $TiCl_4$ treatment was carried out by immersing the TiO_2 electrodes into a 40 mM $TiCl_4$ aqueous solution at $70^\circ C$ for 30 min, followed again by sintering at $500^\circ C$ for 30 min. The sensitization of the TiO_2 electrodes was carried out by their immersion into an industry standard ruthenium dye (N719) ethanolic solution at room temperature for 24 h; 0.2, 0.3 and 0.5 mM dye solutions were tested. PVP electrolytes were cast onto the sensitized working electrodes, while in a low viscosity solution form, for their complete penetration through the voids of mesoporous network. The gelation of electrolytes took place at room temperature for 2 h. Finally, a drop of PVP electrolytic solution was added before the electrodes were sandwiched with counter-electrodes. A hot-melt spacer was used to assemble the solar cells. In all experiments, Pt nanoclusters coated on FTO glasses were used as counter electrodes to DSSCs. The counter electrodes were fabricated by doctor-blading of the PT1 paste on the surface conductive glasses and firing of the system at $500^\circ C$ for 30 min. The fabrication process of the liquid state DSSCs was identical to the ssDSSCs. In all cases, the solar cells active area was 0.25 cm^2 , corresponding to the aperture area of a proper shading mask that covers the rest of the electrode, preventing the light incidence from the edges [35].

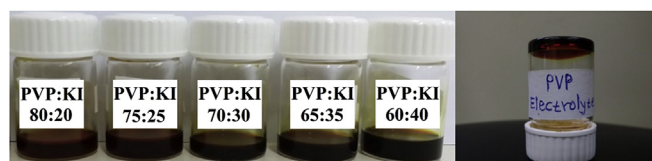


Fig. 1. (left) PVP electrolytes in sealed vessels, (right) quasi-solid state form of PVP electrolytes.

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