Journal of Power Sources 329 (2016) 57–71

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review Article

Absorbency and conductivity of quasi-solid-state polymer electrolytes for dye-sensitized solar cells: A characterization review

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HIGHLIGHTS

- Recent progress in quasi-solid state electrolytes for dye-sensitized solar cells.
- Characterization of quasi-solid state electrolytes.
- Characterizations of absorbency and conductivity.
- Highlighted main outcomes and objectives of each characterizations.

ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form
24 July 2016
Accepted 11 August 2016

Keywords:
Quasi-solid state electrolytes
Gel polymer electrolytes
Polymer electrolytes
Dye-sensitized solar cells
Characterizations

ABSTRACT

The application of quasi-solid state electrolytes for dye-sensitized solar cells opens up an interesting research field to explore, which is evident from the increasing amount of publications on this topic. Since 2010, significant progress has been made with new and more complicated quasi-solid-states materials being produced. The optimization of new materials requires specific characterizations. This review presents a comprehensive overview and recent progress of characterization methods for studying quasi-solid-state electrolytes. Emphasis is then placed on the absorbency and conductivity characterizations. Each characterization will be reviewed according to the objective, experimental set-up, summary of important outcomes, and a few case studies worth discussing. Finally, strategies for future characterizations and developments are described.

1. Introduction

Freely available solar energy is one of the major energy forms that can be harnessed to fulfill future energy needs. The harvesting of solar energy has been introduced in many different technologies. The solar cell is one such technology. Solar cells are typically named after the semiconducting material they are made of, and the number of layers of light-absorbing material, including bulk heterojunction solar cells, depleted heterojunction solar cells, crystalline silicon, thin film, inorganic and organic.

Since the first report in 1991 by Oregan and Gratzel [1], organic dye-sensitized solar cells (DSSCs) are highlighted as promising devices to convert solar energy to electrical energy, due to a prospected low cost, environmentally friendly operation and relatively high efficiency. Inside the DSSC components, the electrodes (mainly the photoanode) are the limiting factors in terms of overall capacity, i.e. efficiency. The electrolyte, on the other hand is not only used to separate the electrodes or to complete the circuit, but acts as a crucial medium to transfer electrons from the counter electrode to the oxidized dye. If the properties of this redox electrolyte are optimized by improving absorbency and ionic conductivity, the efficiency of DSSC will increase too.

Electrolytes used in DSSCs can generally can be classified into three main categories [2]; liquid, quasi-solid-state (QSS) electrolytes and solid-state electrolytes. The usage of liquid electrolytes can cause leaking of the electrolyte, volatilization of the electrolyte, photodegradation of dye and corrosion of the counter electrode. Meanwhile, solid-state electrolytes cause a contact problem at the electrodes. To overcome these shortcomings, researchers have proposed and attempted a technique where both liquid and solid electrolytes are combined, to form a QSS electrolyte.

Although several recent review articles are available about polymer electrolytes based on DSSCs components and cell

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http://dx.doi.org/10.1016/j.jpowsour.2016.08.064
0378-7753/

performance [2–7], materials, preparation and properties of polymer electrolytes [8], and solid polymer electrolytes [9], little attention has been devoted to QSS as one of the main components in DSSCs.

The first application of gel electrolyte in a QSS-DSSC was reported in 1995 [10]. Since then, QSS development has largely been overshadowed by new electrode materials and the emphasis on the power conversion efficiency of DSSCs. To optimize the composition of new materials or to produce commercially standard QSS, the understanding of characterization for these purposes is very important.

Since 2010, much work has been related to the characterization of QSS electrolytes, chiefly regarding materials. This makes them very interesting and attractive, both from the point of view of materials, techniques, basic science and as far as material characterization is concerned. A bibliographic analysis using Web of Science on topics "Quasi Solid State", "Gel", "Electrolyte" and "Solar Cells" showed many publications (240 articles) (Fig. S1). The number of articles is higher in Google Scholar (>8800 articles). Based on these published papers, it is worth reviewing solely the aspect of material characterization.

This review will focus upon the recent progress on the characterization technique of choice for QSS and gel electrolyte evaluation. Also, each characterization technique is followed by a review of related examples. The properties of materials, effect of additive and performance of modification are analyzed according to the capability of the used technique. To cover all QSS and gel electrolytes characterizations would be beyond the scope of this review. Therefore, this review provides selected characterizations in the area of QSS and gel electrolytes for DSSCS over six years (2010–2015). However, a few older papers are also cited to relate the basic understanding and to act as a comparison.

This review is organized into two main characterizations for QSS:

i. Absorbency, visual and liquid loading characterizations: the unique and most important characterization for QSS. An example includes imbibition kinetics.
ii. Electrochemical impedance spectroscopy (EIS) characterizations: characterization of ion transportation mechanism of iodide/tri-iodide (I^-/I_3^-) redox couple in the QSS. Later will discuss in detail as conductivity.

2. Components and mechanism of QSS-DSSCs

The standard configuration and operation principle for a QSS-DSSC involves five main components (Fig. 1a):

i. Anode: a transparent glass substrate covered with a transparent conductive oxide layer, i.e. fluorine-doped tin oxide (FTO).
ii. Photocatalyst: a nanoporous oxide layer, i.e. titanium oxide (TiO_2) deposited on the anode to activate electronic conduction.
iii. Dye: a monomolecule layer charge transfer dye, i.e. N3, N719 and Z709 are covalently bonded to the surface of the mesoporous oxide layer to enhance light absorption. Components of (i)–(iii) are also called photodanode electrode (PE).
iv. Electrolyte: a QSS polymer electrolyte filled with redox mediator, i.e. I^-/I_3^- couple for the recovery of dye and the regeneration of the electrolyte itself during operation.
v. Cathode: a counter electrode (CE) made of a glass substrate coated with a catalyst, i.e. platinum (Pt) to facilitate electron collection.

The anode and cathode are connected through an external circuit, which allows photogenerated electrons to move from the PE to the CE. The QSS can be considered as an electron acceptor (but it does not allow electrons to pass through). All the reactions in QSS involve ionic movement of the I^-/I_3^- couple. The operating principle of DSSC started as the light being transmitted through the CE (the 'p'). The redox electrolyte excites the dye (the 'n'), thus allowing electron transfer though the PE (the 'n') and out to the electrical loop for application.

The subsequent process of oxidized dye to its original reduced species, namely dye regeneration, is mediated via the redox QSS electrolyte (Equations (1), (2) and (3)) in order to complete the circuit loop [11].

$$I^- + I_2 \leftrightarrow I_3^- \qquad [1]$$

$$3I^- + 2\text{dye}^+ \rightarrow I_3^- + 2\text{dye}\ (\text{photoelectrode}) \qquad [2]$$

$$I_3^- + 2e^- \leftrightarrow 3I^- (\text{counter electrode}) \qquad [3]$$

3. What is a quasi-solid-state electrolyte?

A better understanding of the QSS polymer can be related to one of the most common applications, which is used for urine absorption in baby diapers. The swollen gel holds the liquid in a solid, rubbery state and prevents the liquid from leaking onto the skin and clothing. Another common application is as a water-ingredient storage in the agricultural industry. The granules of hydroponic gel absorb the nutrient solution, again releasing this gradually over a long period of time. This type of polymer is normally referred to as 'super absorbent polymer (SAP)' that can absorb and retain extremely large amounts of a liquid relative to their own mass (Fig. 1b). The properties of QSS range from swelling fluid (gel) when agitated to no-flow hard and tough matrix under steady-state conditions (solid). By weight, QSS is mainly liquid, yet it behaves as a solid, owing to a three-dimensional (3D) cross-linked matrix within the liquid electrolyte. In this way, ions are dispersing within a QSS.

'Quasi' solid-state is defined as 'semi' solid electrolyte. It is referring to a physical term as a system that lies along the state between a solid and a liquid. The uniqueness of QSS is related to its solid properties, such as the ability to support their own weight and hold their shape. However, QSS also shares some properties of a liquid. The high ionic conductivity and better interfacial contact are among the important properties of liquid, but are also found in QSS electrolytes. Some QSS are hard elastic and others are very soft, turning to paste when force is applied. Nogueira et al. [12] explained that the main root of a QSS polymer electrolyte is gel polymer electrolyte (GPE). Thus, the definition of QSS is also rooted in a GPE. Polymeric gel is a system that consists of a polymer network swollen with a solvent. Owing to their unique hybrid network structure, gels have both the cohesive properties of solids and the diffusive transport properties of liquids. Gel electrolytes are usually obtained by incorporating a large amount of a liquid plasticizer and/or solvent (containing the desired ionic salts) into a polymer matrix, giving rise to a stable gel with a polymer host structure. When gelation occurs, a dilute or more viscous polymer solution is converted into a system of infinite viscosity: a gel.

The terms 'quasi-solid-state', 'quasi-solid-gel', 'quasi-solid gel-polymer', 'polymer gel', 'jelly-like', 'apparently but not really solid-state', 'gelation' and quasi/gel' are used interchangeably and commonly found in the literature [13–21]. Generally, polymer electrolytes consist of polymer, salt and solvent (solvent for