Carbohydrate Polymers 91 (2013) 682–685

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Novel biopolymer gel electrolyte for dye-sensitized solar cell application

Rahul Singh[a], Nitin A. Jadhav[a], S. Majumder[b], B. Bhattacharya[a,*], Pramod K. Singh[a,*]

[a] Material Research Laboratory, School of Engineering and Technology, Sharda University, Greater Noida 201 310, India
[b] Department of Biotechnology, School of Engineering and Technology, Sharda University, Greater Noida 201 310, India

ARTICLE INFO

Article history:
Received 18 June 2012
Received in revised form 29 July 2012
Accepted 17 August 2012
Available online 28 August 2012

Keywords:
Biodegradable
Electrolyte
IR
SEM
Dye sensitized solar cell

ABSTRACT

We report a new biopolymer electrolyte for dye sensitized solar cell application. To develop polymer electrolyte, potassium iodide have been added in agarose biopolymer matrix and characterized using various techniques like complex impedance spectroscopy, Infrared spectroscopy (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM). Complex impedance spectroscopy shows many folds enhancement in ionic conductivity (σ) by salt doping and conductivity maxima was obtained near 60:40 composition. Infrared spectroscopy confirms the formation of composite nature. XRD revels the reduction of crystallinity by salt doping as well affirms the composite nature. Scanning electron microscopy (SEM) shows reduction in crystallinity of gel matrix by salt doping which is a known favorable condition for ionic conductivity enhancement. To further affirm the conductivity enhancement in the gel electrolyte system a theoretical hopping model is also described in details. A DSSC has been developed using maximum electrical conductivity film which shows 0.54% efficiency at 1 sun condition.

1. Introduction

Gel polymer electrolytes (GPE) are solid ion conductors formed with dissolving salts in polymers having, fitting high molecular weight. They can be prepared in semisolid or solid form, which is a cheap and reliable process when they are manufactured (Choi, Kim, & Ha, 2008; Lenz, 1993; Kumar, Tiwari, & Srivastava, 2012; Ning, Xingxiang, Haihui, & Jianping, 2009). Potential applications for GPE are numerous in devices such as fuel cells, supercapacitors, sensors, electrochromic displays and dye sensitized solar cells (DSSCs). GPEs acquire liquid like conductivity (10^{-2} to 10^{-3} S/cm) which is necessary for electrochemical devices (Alloin, Sanchez, & Armand, 1995; Cheradame, Gandini, Killis, & Nest, 1983; Sato, 1990; Weijia, Xueyi, & Ying, 2011). Our work is focused on developing a dye sensitized solar cell using the biopolymer (agarose) electrolyte. Biopolymer materials, such as chitosan, agarose have been used extensively as electrolytes in electrochemical devices (Kubo, Kitamura, Hanabusa, Wada, & Yanagida, 2002; Nazeeruddin et al., 1993; Wang, Zakeeruddin, Comte, Exnar, & Grätzel, 2003). They are marine algae biopolymers extracted from red seaweed and are hydrophilic in nature. Agarose melts at approximately 85–91 °C, is a polysaccharide (where saccharides are synonimus to carbohydrates) consisting of 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galactopyranose. This basic agarobiose repeat unit forms long chains with an average molecular mass of 120,000 Da, representing about 400 agarobiose units (Rochas & Lahaye, 1989). These polysaccharides serve as the primary structural support for the algae's cell walls. It is environmental friendly and low-cost material that does not require elaborate apparatus to manufacture (Finkenstadt, 2005).

Agar and chitin based GPE electrolytes are well suited for DSSC as electrolyte because in one side they show liquid like conductivity while in other side it assist in wetting the electrolytes (Kaneko, Hoshi, Kaburagi, & Ueno, 2004; Nemoto, Sakata, Hoshi, Ueno, & Kaneko, 2007; Suzuki, Yamaguchi, Kumagai, Tanabe, & Yanagida, 2006).

DSSC (invented by O'Regan and Grätzel in 1991) are now known as third generation photovoltaics since they are very different from the previous semiconductor devices as they do not rely on a traditional p–n heterojunction to separate photogenerated charge carriers. Because of the low-cost materials and easy fabrication, this technology is expected to take a significant share in the fast growing photovoltaic areas. Gel electrolytes are proposed as novel alternative to liquid electrolytes in dye sensitized solar cell (DSSC) application (Bhattacharya, Lee, Geng, Jung, & Park, 2009; Bhattacharya, Tomar, & Park, 2007; Yang et al., 2008). Till to date the maximum stable DSSC reported by Prof. Grätzel group contains liquid electrolyte which has many disadvantages like corrosion, evaporation, volatility, etc. GPE has already proved its suitability in DSSC by providing high electrolytic matrix as well as wetting of working electrode (Singh, Kim, Kim, Park, & Rhee, 2008). In this paper we have developed a new GPE system containing agarose biopolymer doped with potassium iodide. A DSSC has been

---

* Corresponding authors. Tel.: +91 120 2329717; fax: +91 120 2323713.
E-mail addresses: b.bhattacharya@sharda.ac.in (B. Bhattacharya), pramodkumar.singh@sharda.ac.in (P.K. Singh).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.08.055

developed using maximum conducting electrolyte and describe in details.

2. Experimental details

Most of the chemicals used in present study were purified before use in laboratory. Agarose with average molecular weight (M_w = 5000 g/mol) was purchased from HI-MEDIA, Fisher scientific, Mumbai, India while other chemicals like potassium iodide (KI), iodine (I_2) were obtained from Aldrich, USA. Double distilled water (D2) was used as solvent.

In a common preparation method of gel polymer electrolyte (GPE), fixed amount of agarose powder (0.175 g) was dissolved in D2 water (20 ml) in a beaker and continuous stirring at constant heating of 60 °C. This ratio was used as stock solution for overall experiment (written here as B1). Stoichiometric ratio's of potassium iodide (KI) was then dissolved in D2 water (~5 ml.) in another beaker (written here as B2). Adding B2 (drop by drop) in B1 formed clear transparent GPE. These GPE's films were characterized using various techniques. Infrared spectroscopy (Perkin Elmer 883) was carried out to study the composite nature and functional groups present in composite electrolyte. For further confirmation, X-ray diffraction was obtained using Rigaku D/max-2500 in the range of $2\theta = 25\text{–}55°$. For room temperature electrical measurements, GPE's films were placed under the sample holder and connected with CH instrument workstation (model 604D, USA and frequency range 100 Hz to 1 MHz).

DSSC of area 0.25 cm^2 has been developed in our laboratory and details are published elsewhere (Singh, Nagarale, Pandey, Rhee, & Bhattacharya, 2011). The performance of DSSC is evaluated by the current–voltage curve measurements (I–V measurement). The fill factor (FF) is the ratio of the maximum power output (P_{max}) to the product of short circuit photocurrent (I_{sc}) and open circuit voltage (V_{oc}).

$$\mathrm{FF} = \frac{P_{max}}{I_{sc} \cdot V_{oc}} = \frac{I_{mpp} \cdot V_{mpp}}{I_{sc} \cdot V_{oc}}$$

where I_{mpp} and V_{mpp} represent the photocurrent and photovoltage corresponding to the maximal power point, respectively in I–V curve while the energy conversion efficiency (η) is the ratio of P_{max} to the incident radiation power (P_{in}) on the solar cell surface.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc} \cdot V_{oc} \cdot \mathrm{FF}}{P_{in}}$$

3. Results and discussion

3.1. Conductivity measurement

The ionic conductivity of the agarose-based polymer electrolyte film was carried out using CH instrument workstation (model 604D, USA) over frequency range 100 Hz to 1 MHz. To measure ionic conductivity (σ), we have used platinum electrodes and evaluated ionic conductivity using formula

$$\sigma = R_b \left(\frac{l}{A}\right)$$

where σ is ionic conductivity, R_b is the bulk resistance where the Nyquist plot intercepts with the real axis, l is thickness of sample and A is the area of given sample.

The calculated values of ionic conductivity are listed in Table 1 and plotted in Fig. 1. From this table and figure, it was clear that addition of KI in Agar matrix enhances the ionic conductivity and conductivity maxima were obtained at 60:40 compositions. Adding more KI salt the ionic conductivity value goes down. Such an enhancement in ionic conductivity is attributed to the fact that adding KI provided more mobile charge species (K^+ ion and I^- anion) in GPE matrix which enhanced overall ionic conductivity while decrease in ionic conductivity could be explained on the basis of charge pair model (Hashmi, Kumar, Maurya, & Chandra, 1990; Kumar et al., 2012).

Table 1
Calculated values of room temperature ionic conductivity in agarose:KI gel electrolyte system.

Composition (agarose:KI in wt%)	Conductivity (S/cm)
95:5	5.41×10^{-4}
90:10	9.88×10^{-4}
85:15	1.64×10^{-3}
80:20	3.33×10^{-3}
75:25	6.43×10^{-3}
70:30	8.11×10^{-3}
60:40	9.02×10^{-3}
50:50	5.10×10^{-3}

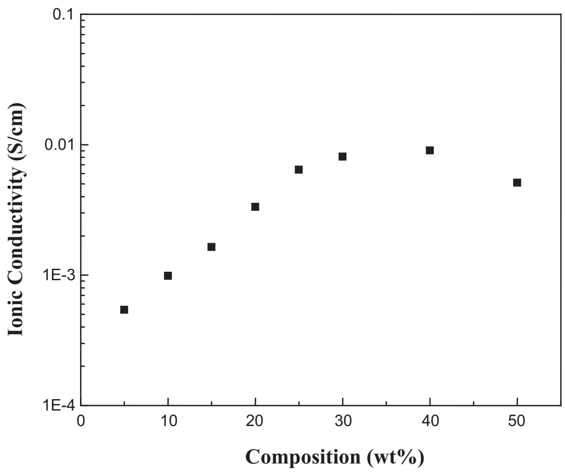

Fig. 1. Conductivity vs. composition (wt% of KI) plot of agarose doped with KI system.

3.2. Infrared spectroscopy

The composite nature of GPE was studied by Infrared spectroscopy (Perkin Elmer 883). Fig. 2 shows the recorded IR spectrum of pure gel (agarose) along with the spectrum of gel doped with potassium iodide (KI, maximum σ composition). The corresponding bands and functional groups are listed in Table 2. It was clear from the figure that almost all the peaks related to host materials (agarose and KI) are present in agarose doped KI sample. Disappearance of any new peaks other than host materials clearly affirms the composite nature of the samples.

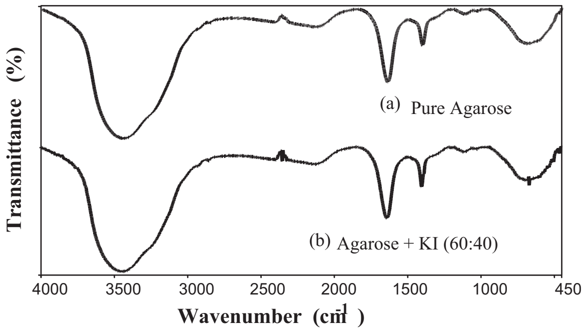

Fig. 2. Infrared spectra of pure agarose and agarose doped with KI sample (60:40) showing maximum conductivity.

Table 2
Infrared spectroscopy bands of a pure agarose and agarose:KI (60:40).

Pure agarose wavelength in cm^{-1}	Agarose:KI wavelength in cm^{-1}	Freq. ranges	Groups (bonds)	Functional groups
3445.86	3434.15	3500–3200 (s, b)	O—H stretch, H— bonded	Alcohols, phenols
2124.66	2105.69	2260–2100 (w)	—CC— stretch	Alkynes
1636.32	1637.57	1650–1580 (m)	N—H bend	Amines
1400.34	1400.22	1500–1400 (m)	C—C stretch	Aromatics
1121.00	1109.07	1250–1020 (m)	C—N stretch	Aliphatic amines
687.28	666.72	700–610 (b, s)	—CC—H: C—H bend	Alkynes
		690–515 (m)	C—Br stretch	Alkyl halides
666.77	545.30	690–515 (m)	C—Br stretch	Alkyl halides

m, medium; w, weak; s, strong; n, narrow; b, broad; sh, sharp.

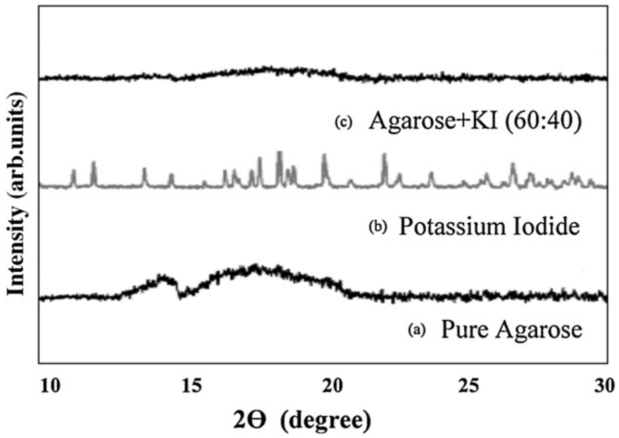

Fig. 3. X-ray diffraction pattern of (a) host gel (agarose), (b) gel with KI (60:40) and (c) pure KI gel polymer electrolyte samples.

To further affirm the composite nature as well as effect of salt concentration, we have recorded the X-ray diffraction pattern (Rigaku D/max-2500) in the range of $2\theta = 25–55^\circ$ with scan rate of 1° min. The recorded X-ray diffraction patterns of host gel (agarose) as well as host gel doped with KI salt are shown in Fig. 3. Pure host gel (agarose) shows a small peak around $2\theta = 16^\circ$ and broad hump at $2\theta = 18–29^\circ$ (Fig. 3a) while potassium iodide XRD spectrum shows well defined crystalline peaks (Fig. 3c). It is clear that a doped gel electrolyte XRD spectrum (Fig. 3b) is free from the peaks related to KI which suggests completely dissolution of KI salt. It is noted that XRD pattern of KI doped gel sample do not contain any additional peaks which clearly affirm the “composite nature” of gel electrolyte system additionally the intensity of the hump decreases by doping KI salt concentration and hump seems almost flat (Fig. 3b). All these information’s clearly affirm that doping salt enhances the amorphous region (suppression of crystallinity) which is well known favorable condition for conductivity enhancement.

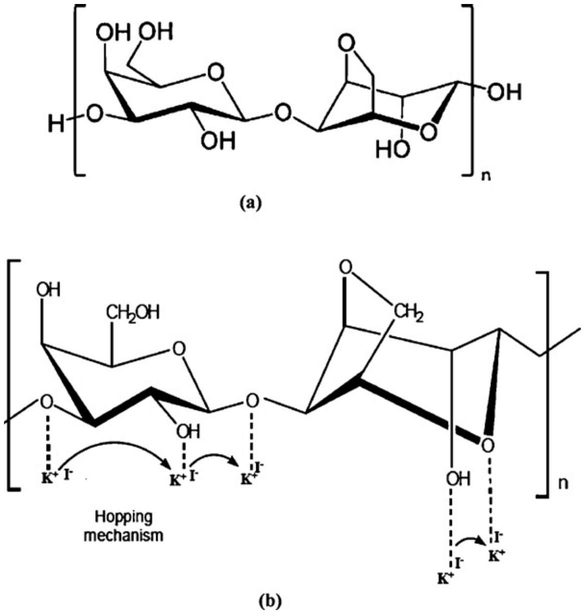

Fig. 5. Chemical structure of agarose (a) and hopping mechanism (b) in agarose:KI gel system.

3.3. Scanning electron microscopy

Scanning electron microscopy (SEM) has been used to further clarify the role of doping of KI salt in GPE matrix. We have recorded SEM micrographs using SEM instrument (SEM, Hitachi S-570) and micrographs are shown in Fig. 4. It is clear that pure gel (agarose) shows well known rough matrix with interconnected gel grains (Fig. 4a). Doping of salt (KI) enhances amorphous matrix and large size pores are clearly viewed in SEM micrograph (Fig. 4b) which is already observed in our XRD data. The conduction mechanism in present gel system is shown in Fig. 5. In present system, potassium

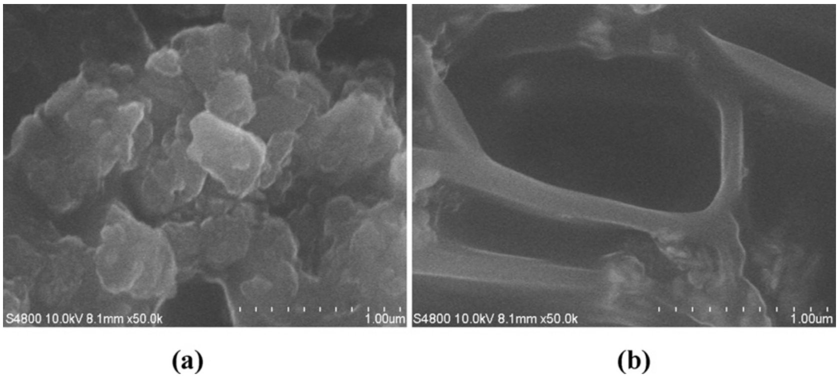

Fig. 4. SEM images of (a) pure agarose and (b) agarose with KI (60:40) samples.

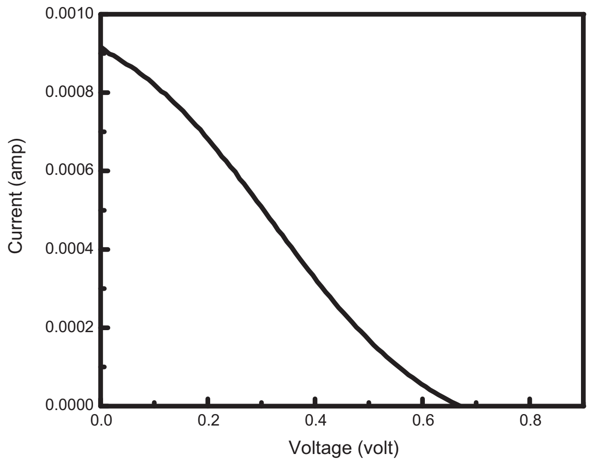

Fig. 6. Current–voltage characteristic of agarose:KI polymer electrolyte film at 1 sun condition.

ion (K^+) and iodide anion (I^-) from KI salt are coordinated with ether oxygen of agarose. Within the matrix the K^+ ion are bounded more rigidly and the I^- are weakly. The weakly bound I^- can easily be dissociated under the influence of a small DC electric field. These I^- ions can hop via each coordinating site as shown in Fig. 5. Similar mechanism could be possible in case of polyiodides generating in dye sensitized solar cell (DSSC) case in polymer electrolyte system containing iodide based redox couple (Koh, Ahmad, & Azmin, 2012).

3.4. DSSC performance

Photovoltaic performance (*I–V* curve) of the DSSC was measured with Keithley 2400 source meter under 1 sun light intensity. The light intensity was adjusted with a crystalline Si solar cell with KG5 filter for approximating 1 sun light intensity. The current–voltage curves for the DSSC employed the Biopolymer electrolyte (maximum conducting) is shown in Fig. 6. The DSSC shows efficiency of 0.54% with short-circuit current density (J_{sc}) of 3.27 mA/cm^2, open circuit voltage (V_{oc}) of 0.670 V and fill factor (FF) of 0.24.

4. Conclusions

Agarose based gel electrolyte doped with KI has been developed and characterized using various techniques. Complex impedance spectroscopic analysis shows that doping of KI provided the additional charge carries (cations/anions) which enhances overall conductivity while decrease in conductivity is due to charge pair formation phenomena. IR as well as XRD confirms composite nature of gel electrolyte. SEM reveals the enhancement in amorphous region of gel electrolyte by KI doping which is further assisted by our XRD data. DSSC using maximum ionic conducting electrolyte shows efficiency of 0.54 at 100 mW/cm^2 light intensity.

Acknowledgement

This work is supported by DST Project, Government of India (SR/S2/CMP-0065/2010).

References

Alloin, F., Sanchez, J. Y., & Armand, M. (1995). New solvating cross-linked polyether for lithium batteries. *Journal of Power Sources*, *54*, 34–39.

Bhattacharya, B., Lee, J. Y., Geng, J., Jung, H. T., & Park, J. K. (2009). Effect of cation size on solid polymer electrolyte based dye-sensitized solar cells. *Langmuir*, *25*, 3276–3281.

Bhattacharya, B., Tomar, S. K., & Park, J. K. (2007). Nanoporous TiO_2 electrode and new ionic liquid doped solid polymer electrolyte for dye sensitized solar cell application. *Nanotechnology*, *18*, 485711–485714.

Cheradame, H., Gandini, A., Killis, A., & Nest, J. F. L. (1983). Mechanism of high ionic conductivity in elastomeric networks. *Journal of Power Sources*, *9*, 389–395.

Choi, M. C., Kim, Y., & Ha, C. S. (2008). Polymers for flexible displays: From material selection to device applications. *Progress in Polymer Science*, *33*, 581–630.

Finkenstadt, V. L. (2005). Natural polysaccharides as electroactive polymers. *Applied Microbiology and Biotechnology*, *67*, 735–745.

Hashmi, S. A., Kumar, A., Maurya, K. K., & Chandra, S. (1990). Proton-conducting polymer electrolyte: The polyethylene oxide + NH_4ClO_4 system. *Journal of Physics D: Applied Physics*, *23*, 1307–1314.

Kaneko, M., Hoshi, T., Kaburagi, Y., & Ueno, H. (2004). Solid type dye-sensitized solar cell using polysaccharide containing redox electrolyte solution. *Journal of Electroanalytical Chemistry*, *572*, 21–27.

Koh, J. C. H., Ahmad, Z. A., & Azmin, A. A. (2012). Bacto agar-based gel polymer electrolyte. *Ionics*, *18*, 359–364.

Kubo, W., Kitamura, T., Hanabusa, K., Wada, Y., & Yanagida, S. (2002). Quasi-solid-state dye-sensitized solar cells using room temperature molten salts and a low molecular weight gelator. *Chemical Communications*, 374–375.

Kumar, M., Tiwari, T., & Srivastava, N. (2012). Electrical transport behaviour of bio-polymer electrolyte system: Potato starch + ammonium iodide. *Carbohydrate Polymers*, *88*, 54–60.

Lenz, R. W. (1993). Biodegradable polymer. *Advances in Polymer Science*, *107*, 1–40.

Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Müller, E., Liska, P., et al. (1993). Conversion of light to electricity by cis-X2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge-transfer sensitizers ($X = Cl^-$, Br^-, I^-, CN^-, and SCN^-) on nanocrystalline titanium dioxide electrodes. *Journal of American Chemical Society*, *115*, 6382–6390.

Nemoto, J., Sakata, M., Hoshi, T., Ueno, H., & Kaneko, M. (2007). All-plastic dye-sensitized solar cell using a polysaccharide film containing excess redox electrolyte solution. *Journal of Electroanalytical Chemistry*, *599*, 23–30.

Ning, W., Xingxiang, Z., Haihui, L., & Jianping, W. (2009). N,N-dimethylacetamide/lithium chloride plasticized starch as solid biopolymer electrolytes. *Carbohydrate Polymers*, *77*, 607–611.

Rochas, C., & Lahaye, M. (1989). Average molecular weight and molecular weight distribution of agarose and agarose-type polysaccharides. *Carbohydrate Polymers*, *10*, 289–298.

Sato, H. (1990). Theoretical background for the mixed alkali effect. *Solid State Ionics*, *40–41*, 725–733.

Singh, P. K., Kim, K. W., Kim, K. I., Park, N. G., & Rhee, H. W. (2008). Nanocrystalline porous TiO_2 electrode with ionic liquid impregnated solid polymer electrolyte for dye sensitized solar cells. *Journal of Nanoscience and Nanotechnology*, *8*, 5271–5274.

Singh, P. K., Nagarale, R. K., Pandey, S. P., Rhee, H. W., & Bhattacharya, B. (2011). Present status of solid state photoelectrochemical solar cells and dye sensitized solar cells using PEO-based polymer electrolytes. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, *2*, 023002–0203015.

Suzuki, K., Yamaguchi, M., Kumagai, M., Tanabe, N., & Yanagida, S. (2006). Dye-sensitized solar cells with ionic gel electrolytes prepared from imidazolium salts and agarose. *Comptes Rendus Chimie*, *9*, 611–616.

Wang, P., Zakeeruddin, S. M., Comte, P., Exnar, I., & Grätzel, M. (2003). Gelation of ionic liquid-based electrolytes with silica nanoparticles for quasi-solid-state dye-sensitized solar cells. *Journal of American Chemical Society*, *125*, 1166–1167.

Weijia, W., Xueyi, G., & Ying, Y. (2011). Lithium iodide effect on the electrochemical behavior of agarose based polymer electrolyte for dye-sensitized solar cell. *Electrochimica Acta*, *56*, 7347–7351.

Yang, H., Huang, M., Wu, J., Lan, Z., Hao, S., & Lin, J. (2008). The polymer gel electrolyte based on poly(methyl methacrylate) and its application in quasi-solid-state dye-sensitized solar cells. *Material Chemistry and Physics*, *110*, 38–42.