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Electrical, structural, and thermal properties of succinonitrile-LiI-I_2 redox-mediator

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ABSTRACT

We synthesized a solid $I^-/I_3{}^-$-based redox-couple electrolyte using a mixture of succinonitrile, LiI and I_2. An increase of LiI to succinonitrile mole ratio (x) up to 2.5% led to a fast rise in the electrical conductivity ($\sigma_{25^\circ C}$) of the electrolytes. Further increase in x slowly increased the $\sigma_{25^\circ C}$-value. The composition with x = 5% achieved the highest $\sigma_{25^\circ C}$-value ($\sim 1.6 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$) and was referred to as the optimum conducting composition (OCC) of the electrolytes. Also, an increase of x led to a decrease of the melting temperature of the electrolytes as suggested by the $\log\sigma - T^{-1}$ study and ascertained by the differential scanning calorimetry study. The $\log\sigma - T^{-1}$ study showed a linear trend before and after the melting temperature, and the activation energy increased with increasing x-value. The electrical and thermal properties were explained using the vibrational spectroscopy study. The ionic transference number measurement showed that the electrolytes with x = 4 and 5% are predominantly ionic in nature.

1. Introduction

Renewable energy sources are currently highly demanding because of the environmental issues. The high rise of levels of greenhouse gases and pollution especially in developed and developing countries is leading to a potential mass destruction of the humankind through negative environmental effects. One of the renewable energy sources, the solar cell, is highly useful in a country like Saudi Arabia, where solar irradiance is quite high [1]. The dye-sensitized solar cell (DSSC), a third-generation solar cell, offers simple cell structure and cost-effectiveness in materials and manufacturing as compared to other solar cells [2]. Short energy payback time (< 1 year), enhanced performance under real outdoor conditions and capturing of light from all angles of the incident are some of the interesting features of the DSSCs. In the conventional DSSC, an $I^-/I_3{}^-$-based redox-couple liquid electrolyte is used for dye regeneration at the working electrode (WE; mesoporous TiO_2 layer) [2,3]. The dye regeneration occurs via oxidation of I^- producing $I_3{}^-$. The reduction of $I_3{}^-$ into I^- occurs at the counter electrode (platinum layer). A fast diffusion of redox-couple is required for the efficient cell operation [3]. At present, the highest cell efficiency, η ~ 11.1%, is reported for the liquid electrolyte: 0.6 M dimethyl propyl imidazolium iodide, 0.1 M LiI, 0.05 M iodine, and 0.5 M tert-butylpryidine (TBP) in acetonitrile [4]. The mixture, LiI-I_2 produces $I^-/I_3{}^-$-redox-couple in the solution. The additive, TBP generally helps to increase the open circuit voltage of the cell by shifting the WE's conduction band towards higher energy. A use of imidazolium ionic liquid helps to increase the electrical conductivity and decrease the evaporation rate of the acetonitrile. A use of liquid electrolyte makes the cell prone to leakage of solvent especially at elevated operating temperature conditions due to the internal pressure. It also creates scale-up problem of manufacturing. The cell requires hermetic sealing too. Therefore, a solid electrolyte is required to meet the harsh environmental conditions as observed in gulf countries. For a review, see references, [2,3,5].

Succinonitrile (SN; $N{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}N$) is a non-ionic and low-molecular-weight plastic crystal, which has a plastic crystal phase between −38 °C (crystal to plastic crystal phase transition temperature, T_{pc}) and 58 °C (melting temperature, T_m) allowing a high molecular diffusivity via increasing concentration of trans isomers and molecular jumps from one diagonal position of the cubic structure to another [6–8]. Because of its low T_m-value, high dielectric constant (~55) and waxy nature, succinonitrile also acts as a solid solvent/plasticizer to prepare redox-couple solid or gel electrolytes for dye-sensitized solar cells. Until now, succinonitrile has been used either with an ionic liquid [9–19], an organic iodide salt [13,14,20], an inorganic iodide salt [19], or with a polymer matrix [21–29] in the following composition: SN (with or without a polymer matrix)-XI-I_2. Here, the notation, X,

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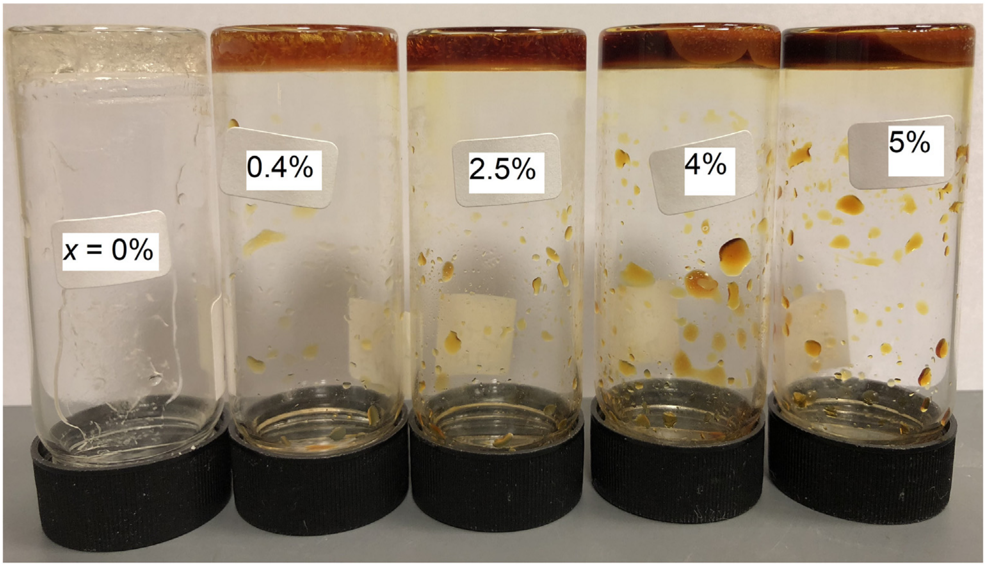

Fig. 1. SN-LiI-I_2 electrolytes (x = 0–5%) at room temperature (25 °C).

represents a cation of an ionic liquid, an organic salt, or an inorganic salt. Wang et al. [9] have used an ionic liquid, *N*-methyl-N-butylpyrrolidinium iodide to prepare a solid electrolyte, which exhibited $\sigma_{25^\circ C}$ of 3.3×10^{-3} S cm^{-1}, apparent diffusion coefficients of 3.7×10^{-6} and 2.2×10^{-6} cm^2 s^{-1} for I^- and $I_3{}^-$, respectively, and η of 6.5% at 1 sun. Since then, numerous ionic liquids were used, which are as follows: *N*-dimethyl-N-propyl-N-butylammonium iodide [13], ethyl methyl imidazolium iodide [13], dimethyl imidazolium iodide [13], ethyl methyl pyrrolidinium iodide [13], 1-butyl-3-methylimidazolium tetrafluoroborate [14], 1-vinyl-3-methylimidazolium iodide [15], 1-vinyl-3-ethylimidazolium iodide [15], 1-vinyl-3-butylimidazolium iodide [15], 1-methyl-3-acetylimidazolium iodide [16], 1-ethyl-3-methylimidazolium iodide [16], 1-propyl-3-methylimidazolium iodide [16],1-methyl-3-propylimidazolium iodide (MPII) [17], 1-methyl-3-butylimidazolium iodide [17], 1-alkyl-2,3-dimethylimidazolium iodide [18], 1,2-dimethyl-3-propylimidazolium iodide [19], and 1-butyl-3-methylimidazolium iodide [19]. The WE structure was also modified by several research groups in order to improve the cell efficiency [10–12]. Dai et al. [13,20] thoroughly studied electrical, diffusion and thermal properties of tetrabutylammonium iodide (TBAI)-and tetraethylammonium iodide (TEAI)-based electrolytes. The former electrolyte exhibited better electrical conductivity and diffusion coefficients. The DSSC based on the TBAI electrolyte showed cell efficiency of 5% [14]. Gupta et al. [21–25] showed that a blend of SN and poly(ethylene oxide) in equal weight proportion can be used as a polymer matrix to prepare fast ion conducting solid electrolytes. In the blend-MI-I_2 (M = Li or K) electrolytes, the K^+ ions-based electrolyte exhibited better electrical conductivity than the Li^+ ions-based electrolyte; however, the later showed better photovoltaic properties [26]. Hwang et al. [27] prepared (SN-polyacrylonitrile)-1-propyl-2,3-dimethylimidazolium iodide-I_2-*N*-methyl benzimidazole electrolyte-based DSSC and reported cell efficiency of 3.3%. The efficiency was further improved to 7.6% by using a hierarchical structure of the WE [27]. Zhu et al. [28] showed cell efficiency of 4.4% using an (SN-neopentylglycol)-MPII-LiI-I_2-TBP electrolyte ($\sigma_{25^\circ C} \sim 2.1 \times 10^{-3}$ S cm^{-1}). A (polyethylene glycol-SN-thiourea)-TiO_2-KI-I_2 electrolyte solution was also used in the DSSC, which exhibited η of 2.38% at 1 sun [29].

Byrne et al. [19] synthesized an SN-LiI-I_2 electrolyte in 100:5:1 mol ratio and fabricated a DSSC, which exhibited η of 3.58% at 1 sun. They used LiI because Li^+ ions are known to adsorb/interact well on/with the dye-sensitized TiO_2 layer, thereby they found an increase in electron injection rate and unfortunately a decrease in the TiO_2's conduction band edge [19,26]. However, they did not study the electrical, structural, and thermal properties of the SN-LiI-I_2 electrolyte. Therefore, in the present study, we have concentrated only on electrical, structural, and thermal properties of the SN-LiI-I_2 electrolyte. We have optimized the electrical conductivity ($\sigma_{25^\circ C}$) of the SN-LiI-I_2 electrolytes via varying LiI-to-SN mole ratio (x) from 0 to 5%. The electrolytes with compositions, $x > 5\%$ were inhomogeneous in nature. The electrical conductivity is determined with temperature in order to determine the nature of ion transport and the activation energy. Ionic transference number (t_{ion}) is measured to determine the ionic contribution to the total electrical conductivity of the electrolyte. The electrical transport properties are explained using the vibrational spectroscopy study. We have also carried out the differential scanning calorimetry (DSC) for determining the melting temperature of the electrolytes exactly as suggested by the vibrational spectroscopy and $\log\sigma - T^{-1}$ studies.

2. Experimental details

2.1. Electrolyte preparation

Succinonitrile, LiI, and I_2, all from the Sigma-Aldrich chemicals, were used without further purification. A mixture of succinonitrile, LiI, and I_2 in a glass vial was first kept at ~70 °C in an oven for a few minutes to melt the succinonitrile and then stirred at ~60 °C for 24 h, which resulted in a homogeneous redox-couple electrolyte. The LiI-to-succinonitrile mole ratio (x) was varied from 0 to 5%. The I_2-to-LiI mole ratio was kept equal to 10%. As shown in Fig. 1, the electrolytes were solid at room temperature.

2.2. Electrolyte characterizations

For the electrical conductivity measurement, the melted electrolyte solution was poured at the 0.5-mm thick space between platinum electrode plates (active area ~16 mm^2) of a specially designed sample holder kept at ~70 °C in an oven. The sample holder is shown in Fig. 2. After cooling at room temperature, a complex impedance curve was acquired in a frequency range of 10–10^5 Hz with ac amplitude of 20-mV using a HIOKI IM 3533-01 LCR meter. The electrical conductivity was calculated using an expression, $\sigma = t/(a\,R)$, where t is spacing between platinum electrode plates, a is an active area of electrode plates, and R is a resistance of the complex impedance curve intersecting at the real axis. For the log σ − T^{-1} study, the sample holder was kept in a digitally temperature-controlled oven. The actual electrolyte temperature was determined using a digital thermometer attached to the sample