

**Review Report on Ionic Conductor with High Conductivity as
Single-Component Electrolyte for Efficient Solid-State Dye-
Sensitized Solar Cells**

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ABSTRACT

In solid state dye sensitized solar cells (ssDSSCs), imidazolium iodides and their polymers are used as ionic conductor. Relay-type Grotthus mechanism and lamellar structure improve the conductivity of single component solid state electrolyte and enhance the efficiency of ssDSSCs. This study designed and synthesized salts of imidazolium or piperidinium with a pendent propargyl group as the single component solid state electrolyte. Single component solid-state electrolyte-based ssDSSC with an organic dye showed power conversion efficiency of 6.3% under simulated AM1.5G illumination (100 mW cm^{-2}) and exhibited good long-term stability under continuous 1 sun soaking for 1500 h.

INTRODUCTION

Among photovoltaic devices, Dye-sensitized solar cells (DSSCs) play major to produce direct current with efficiency over 12% with volatile organic liquid as electrolyte. Typical DSSCs consist of electrode, counter electrode and electrolyte where dye sensitized nano crystalline TiO_2 film is used to produce working electrode, Pt-coated conductive glass for counter electrode, and the redox couple I^-/I_3^- in a volatile organic solvent as the electrolyte. But these volatile organic solvents limit the outdoor applications due to its evaporating ability. To overcome this problem, quasi liquid and solid state electrolytes emerge as a solution. There few types of solid state electrolytes such as p-type inorganic semiconductors (CuI, CuSCN, etc.),¹ organic hole-transporting materials,²⁻⁴ and ionic conductors.

In solid state dye sensitized solar cells (ssDSSCs), imidazolium iodides and their polymers are used as ionic conductor. but ionic conductors have relatively low conductivity in general. Therefore without any additives in the solid electrolyte or post-treatments on the ssDSSCs shows much less efficient when compared with ssDSSCs which have additives in the solid electrolyte or post-treatments on the dye sensitized films. Although Doping of iodine and LiI, improve the conductivity and photovoltaic performance of ionic conductor, this may also associate with negative effects such as charge recombination and incident light filtering.⁵ additives enhance the conductivity of ssDSSCs and some examples for additives used in ionic conductors are (p- BrC_6H_4) $_3\text{NSbCl}_6$ or Co(III) complexes doped in 2,2',7,7'-tetrakis (N,N-di-p methoxyphenylamine) -9, 9'-spirobifluorene (spiro-MeOTAD)5,10 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ doped in

PEDOT⁶. Adding additives or doing some treatment improves the conductivity but it also enhances the complexity of the system. The main aim of this study was to develop a single component solid state electrolyte with high conductivity and enhance the outdoor application of ssDSSCs.

Relay-type Grotthus mechanism and lamellar structure improve the conductivity of single component solid state electrolyte and enhance the efficiency of ssDSSCs. This study designed and synthesized salts of imidazolium or piperidinium with a pendent propargyl group (PMIm and PMPi, Figure 1a) as the single component solid state electrolyte. And this PMIm and PMPi shows greater conductivity without any additives or post treatment beside these compounds have higher conductivity when compared with alkyl-substituted imidazolium iodide.

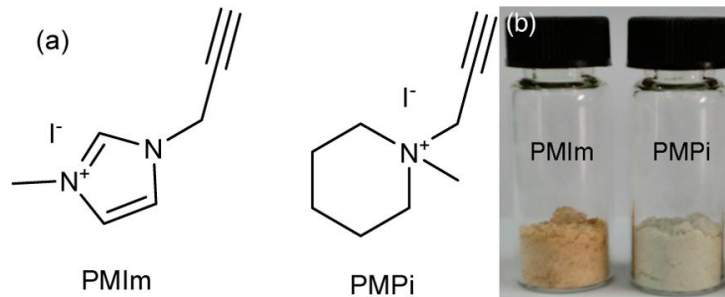


Figure 1. Structures of the propargyl-functionalized ionic conductors (a) and their photograph (b).

This single component solid-state electrolyte-based ssDSSC with an organic dye (MK2, Figure 2)⁷ achieved power conversion efficiency of 6.3% under simulated AM1.5G illumination (100 mW cm⁻²) and exhibited good long-term stability under continuous 1 sun soaking for 1500 h.

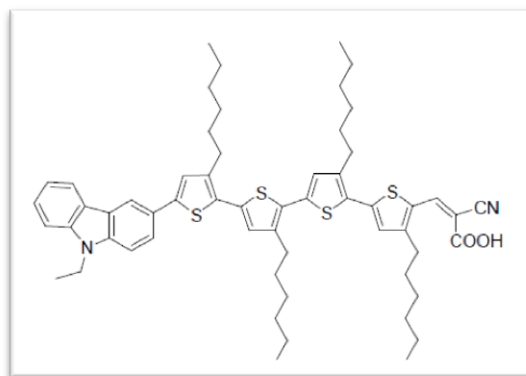


Figure 2: Chemical structure of the metal-free organic dye (MK2)

RESULTS AND DISCUSSION

Propargyl-functionalized, PMIm and PMPi ionic conductors are solid state below 80 °C and dissolve with common organic liquid such as methanol and ethanol. Therefore it is an advantageous for solid state electrolyte filling in ssDSSCs.

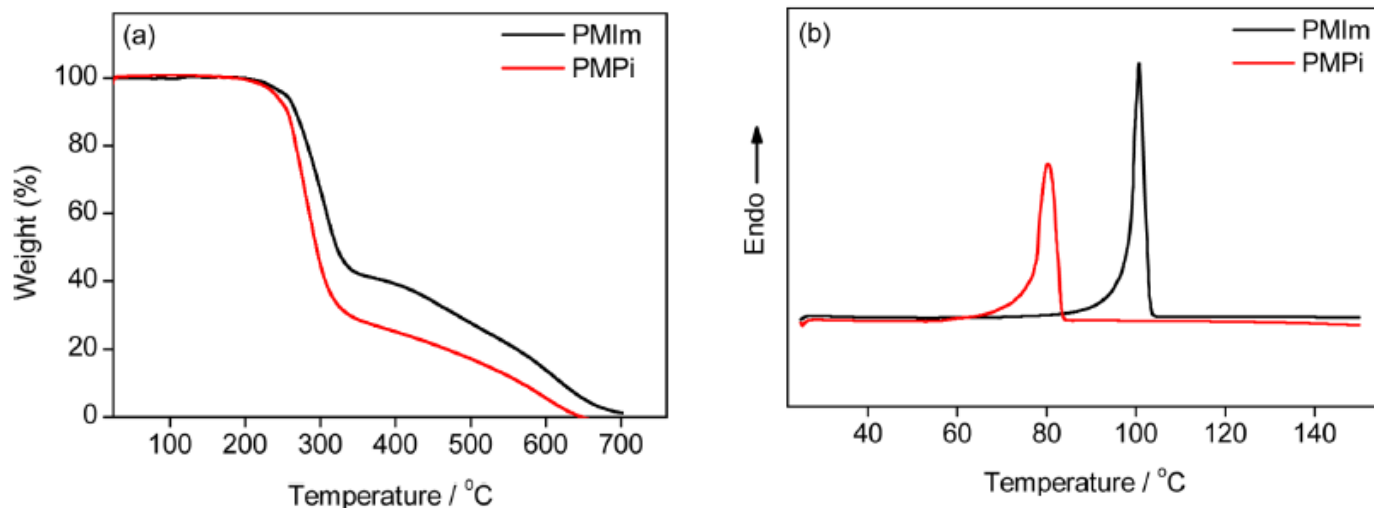


Figure 3. TGA curves (a) and DSC curves (b) of the as-prepared propargyl-functionalized ionic conductors.

Figure 3a shows the Temperature degradation curve for PMIm and PMPi and decomposed start at 245 and 224 respectively. These is good indication for these Propargyl-functionalized, PMIm and PMPi ionic conductors can use to outdoor application because its shows very good thermal stability under 200 °C. Figure 3b. Show the DSC curves and give the information about phase transition from solid to liquid of two Propargyl-functionalized ionic conductors where the melting point of PMIm and PMPi were 100 and 80 °C respectively. Again this confirms

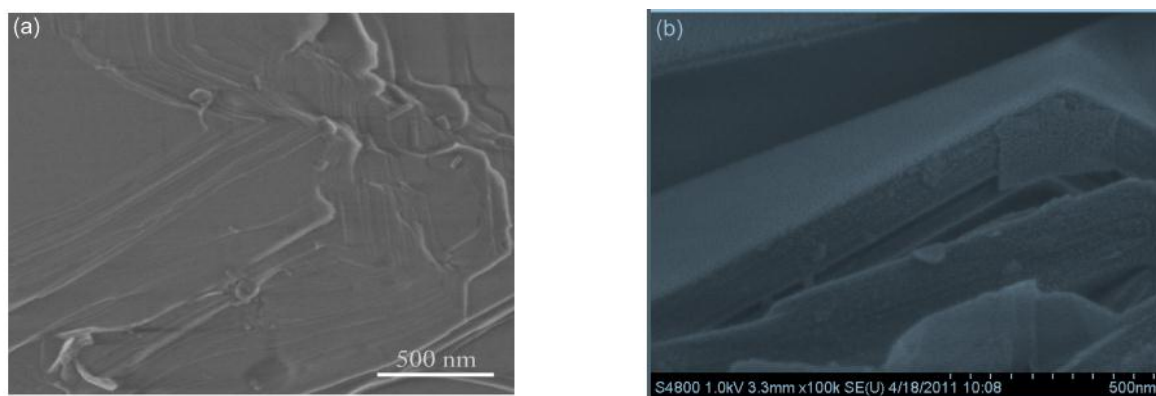


Figure 4. FESEM images of PMIm (a) and PMPi (b).

Propargyl-functionalized, PMIm and PMPi ionic conductors are very suitable candidates for outdoor applications. Figure 4 reveals the lamellar structure of Propargyl-functionalized ionic conductors by using FESEM.

Table 1. Conductivity for the Propargyl-Functionalized Ionic Conductors and Photovoltaic Performance Parameters of ssDSSCs with Them as Solid-State Electrolytes

| solid electrolyte | $\sigma/\text{mS cm}^{-1}$ | $J_{sc}/\text{mA cm}^{-2}$ | V_{oc}/V | FF | $\eta/\%$ |
|-------------------|----------------------------|----------------------------|-------------------|------|-----------|
| PMIm | 40 | 12.65 | 0.71 | 0.70 | 6.3 |
| PMPi | 9 | 5.21 | 0.66 | 0.65 | 2.2 |
| DMPImI | 1.0×10^{-3} | 0 | 0 | 0 | 0 |

Table 1 shows that PMIm has the highest conductivity than that of PMPi and DMPImI at room temperature. This is explained by using the smaller interlayer distance and better crystallinity for PMIm as compared to PMPi. More importantly, the conductivity of PMIm was as high as 40 mS cm^{-1} at room temperature, which was even higher than that (25 mS cm^{-1}) for the solution of $0.4 \text{ M LiI} + 0.04 \text{ M I}_2$ in acetonitrile.⁸ To explain the effect of the propargyl group on the conductivity, they used another ionic conductor to compare PMIm with 1,2-dimethyl-3-propylimidazolium iodide (DMPImI, solid state at room temperature). Table 1 reveals that introduction of propargyl to the imidazolium ring enhanced the conductivity by 40000-fold. This indicates that Propargyl-Functionalized Ionic Conductors have very high conductivity.

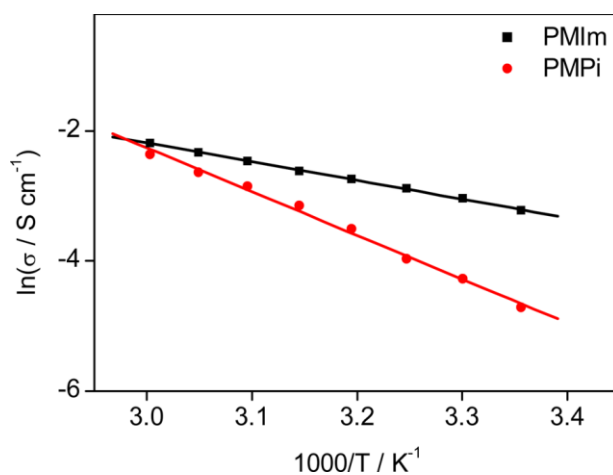


Figure 5. Temperature dependence of the ionic conductivity for the two propargyl-functionalized ionic conductors.

From figure 5 It can be seen that conductivity rises with temperature. The data in Figure 5 can be fitted well by the Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

Where σ_0 is a constant, E_a the activation energy, k Boltzmann's constant, and T the absolute temperature. The data fit to the linear dependence of $\ln \sigma$ on $1/T$. which is indication of conductivity of propargyl-functionalized ionic conductors are obey the relay-type Grotthus mechanism and accredited to ionic conduction and this is started from the charge transfer along the polyiodide chain.

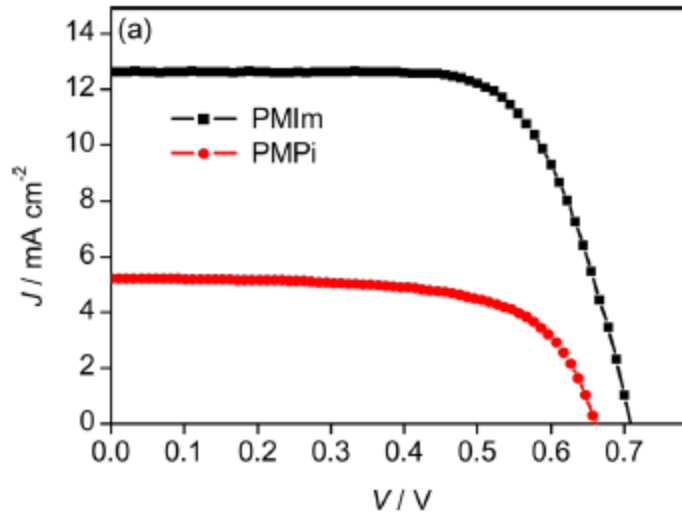


Figure 6. Photocurrent density–voltage characteristics.

ssDSSCs with these propargyl-functionalized ionic conductors as single-component solid electrolytes were evaluated under illumination of AM1.5G simulated solar light (100 mWcm^{-2}). Figure 6 shows the J–V curves with the corresponding photovoltaic data summarized in Table 1. PMIm produced η of 6.3% ($J_{sc} = 12.65 \text{ mA cm}^{-2}$, $V_{oc} = 0.71 \text{ V}$, $FF = 0.70$), while PMPi produced η of 2.2% ($J_{sc} = 5.21 \text{ mA cm}^{-2}$, $V_{oc} = 0.66 \text{ V}$, $FF = 0.65$). PMIm generated much higher J_{sc} than PMPi since the former has a higher conductivity than the latter. For DMPImI, which has a very low conductivity, it cannot generate photocurrent (Table 1).

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