Synthesis of alkylimidazolium thiocyanate molten salts and its application to the solid-state dye-sensitized photovoltaic cells using CuI as a hole collector

Akinori Konno,[†] Fumiaki Okutsu,[†] Hiroaki Kida,[†] G. R. Asoka Kumara,[†] and Kirthi Tennakone[‡]
[†]Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432-8561 Japan.
[‡]Institute of Fundamental Studies, Hantana road, Kandy, Sri Lanka.

Room temperature molten salts constitute promising systems with the potential of practical applications in a diverse variety of technological disciplines.[1] Organic electrochemical applications of these materials have intensively been studied especially for environmentally friendly alternative to the conventional organic electrolytic medium, i.e. supporting electrolyte and organic solvent. A class of room temperature molten salt that has been widely studied are the salts formed from imidazolium derivatives and inorganic or organic acids. An interesting observation we made was the peculiar behavior of the thiocyanate ion. Some alkylammonium thiocyanates were also reported to show quite low melting points.[2] On the other hand, we have reported successful application of one of these thiocyanates, i.e. 1-ethyl-3-methylimidazolium thiocyanate (EMISCN), to the dye-sensitized solid-state solar cell, as an additive and a crystal growth inhibitor for CuI layer preparation.[3] The preparation of novel room temperature molten thiocyanate salts and their preliminary application to the solid-state dye-sensitized photovoltaic cells (DSSSCs) were also reported previously.[4] In this paper, development of novel room temperature molten thiocyanate salts and their effect on the performance of DSSSCs are presented in detail.

1-Alkyl-3-methylimidazolium thiocyanates were prepared by the reaction of corresponding imidazolium iodide with AgSCN. It is noted that this reaction was greatly promoted by microwave irradiation and completed within 2-3 min. All of them resulted in the formation of room temperature molten thiocyanates (Table 1). The imidazolium thiocyanate which have shorter alkyl chain length showed lower melting point. The conductivity decreased with length of alkyl chain in imidazolium cation.

We investigated the effect of these thiocyanates as an additive in CuI layer of DSSSC. I-V characteristics of TiO_2/Dye/CuI cell with the addition of a variety of thiocyanate (4.5 mol%) to CuI layer, are shown in figure 1 and table 2. It is notable that the addition of the imidazolium thiocyanates having shorter alkyl chain showed better performance of TiO_2/Dye/CuI DSSSCs than that having longer alkyl chain. Since the addition of long alkyl chain imidazolium thiocyanate to CuI seems to decrease the conductivity of CuI layer, it is reasonable that Isc decreased in the cases of 6IT or 9IT addition compared with the case of 2IT. However, it is difficult to explain the changes in Voc and fill factor. The results of other molten thiocyanates will be also discussed.

References
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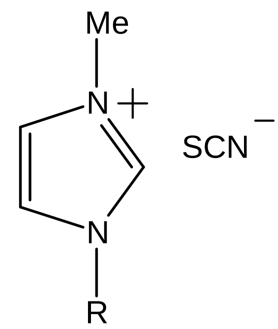
Table 1. Properties of alkylimidazolium thiocyanates.



Thiocyanate	m.p./°C	Conductivity[a] log (σ / Scm^{-1})
2IT (R = C_2H_5)	-80	-1.83
6IT (R = C_6H_{13})	-78	-1.64
9IT (R = C_9H_{19})	-68	-1.41

[a] Measured at 25 °C.

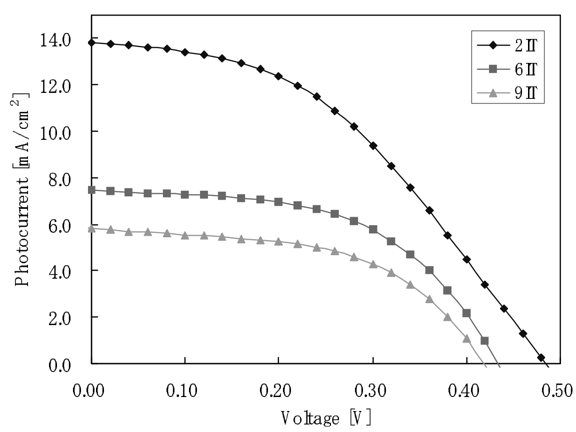


Figure 1. I-V characteristics of TiO_2/N3 dye/CuI cells with the addition of imidazolium thiocyanate to the CuI layer.

Table 2. Solar cell performance of TiO_2/N3 dye/CuI DSSSCs with the addition of a variety of thiocyanate (4.5 mol%) to CuI layer.

thiocyanate	Voc / V	Jsc / mAcm^{-2}	Fill Factor	Efficiency / %
2IT	0.49	13.8	0.42	2.9
6IT	0.43	7.5	0.53	1.7
9IT	0.42	5.8	0.53	1.3