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Binary counter ion effects and dielectric behavior of iodide ion conducting gel-polymer electrolytes for high-efficiency quasi-solid-state solar cells

T. M. W. J. Bandara,^a S. L. N. Senavirathna,^c H. M. N. Wickramasinghe,^a
K. Vignarooban,^c L. A. De Silva,^d M. A. K. L. Dissanayake,^e I. Albinsson^f and
B.-E. Mellander^b

A series of highly efficient quasi-solid-state dye-sensitized solar cells (DSCs) is prepared by harnessing the binary cation effect and positive effects of the selected performance enhancers of gel-polymer electrolytes. The new electrolyte is composed of polyacrylonitrile polymer, tetra-hexylammonium iodide (Hex₄NI) and KI binary salts as well as 4-*tert*butylpyridine and 1-butyl-3-methylimidazolium iodide performance enhancers. The charge transport in the series of electrolytes is thermally activated and, accordingly, the temperature dependence of conductivity follows the VTF behavior. The enhancement of conductivity is observed with an increasing mass fraction of KI and decreasing mass fraction of Hex₄NI, while the total mass fraction of salts in the electrolyte is kept unchanged. The highest conductivity of 3.74 mS cm⁻¹ at ambient temperature is shown by the sample containing KI only (without Hex₄NI) at all the temperatures. The effects of dielectric polarization of the electrolytes are studied by analyzing the frequency dependence of the real and the imaginary parts of the AC conductivity in detail. Appropriate and reproducible cell construction are assured by efficiencies of above 5% exhibited by all the quasi-solid-state DSCs assembled using double-layered TiO₂ photo-electrodes and the new electrolyte series. Besides, highlighting the mixed cation effect, the cells with mixed salts exhibited efficiencies greater than 6%. An impressively high efficiency of 7.36% was shown by the DSC prepared with electrolyte containing 75 wt% KI and 25 wt% Hex₄NI. This study reveals that the salt combination of KI and Hex₄NI, which has not been reported before, is a suitable binary iodide salt mixture to prepare highly efficient DSCs. The replacement of tetra-hexylammonium ions by K⁺ ions improves the charge transport in the electrolyte; however, the best solar cell performance is shown by the mixed salt system with 75 wt% KI and 25 wt% Hex₄NI, which is not the highest conductivity composition. Therefore, the exhibited high efficiency of 7.36% is evidently due to the binary cation effect.

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1. Introduction

The possibility of using gel-polymer electrolytes to enhance chemical and physical stability in dye-sensitized solar cells (DSCs) has been demonstrated since the beginning of the last two decades.^{1–3} Recently, dye-sensitized solar cells (DSCs) based on gel-polymer electrolytes (GPEs) have gained a significant advancement over their liquid electrolyte counterparts.^{1,4–6} It is well known that the liquid electrolytes, generally used in DSCs,

ensure higher ionic conductivities and thus improve the cell efficiency, but they are still prone to chemical and physical instability.^{7,8} The disadvantages of liquid electrolytes include the lack of long-term stability due to the liquid leakage, sealing difficulties, flammability issues, corrosion of counter electrode, dye degradation, photo-degradation of constituting materials and photodecomposition of the dye in the solvent medium.

In contrast, quasi-solid-state DSCs based on GPEs have a great advantage over the aforesaid limitations. Numerous studies have been reported on finding suitable GPEs for DSCs, mainly focusing on replacing unstable liquid electrolytes by more stable gel (or quasi-solid state) polymer electrolytes.^{1,9} One of the conventional ways to improve the efficiency in a DSC based on a polymer electrolyte is the incorporation of plasticizers such as propylene carbonate (PC) into the electrolyte. However, since the presence of an excessive amount of solvent in the

^a Department of Physics and Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka. E-mail: awijendr@yahoo.com

^b Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

^c Department of Physics, University of Jaffna, Jaffna, Sri Lanka

^d Department of Physics, University of West Georgia, Carrollton, USA

^e National Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

^f Department of Physics, University of Gothenburg, Gothenburg, Sweden

electrolyte transforms it into a viscous liquid, there is an upper limit to the solvent content to keep the electrolyte in the gel state. The present work focuses on improving DSC performance by capitalizing on the mixed counter ion effect without degrading the gel nature of the electrolyte. The work is extended to study the effects of the polarization in electrolytes by analyzing the frequency dependence of both real and imaginary parts of the AC conductivity in detail since such data is important, but is lacking in the literature.

1.1 Polyacrylonitrile based GPEs

Interfacial characteristics and mechanical stability of polyacrylonitrile (PAN) based GPEs are favorable for the functioning of the devices based on gel electrolytes.^{10–12} PAN has been successfully utilized as a host polymer matrix in Li⁺ ion conducting GPEs as an electrolytic membrane for high energy density rechargeable lithium-ion batteries and photo-electrochemical solar cells.^{10,13,14} DSCs prepared with PAN have exhibited higher energy conversion efficiencies of about 7.27%.^{9,15} Therefore, in the present work, PAN was selected as the host polymer to exploit its positive effect by the preparation of a series of quasi-solid-state electrolytes.

In PAN-based GPEs, it is generally accepted that the electrolytic solution, formed by dissolving the ionic salt in an ethylene carbonate (EC) and propylene carbonate (PC) co-solvent, is “entrapped” in cages formed by the PAN polymer matrix making the electrolyte exhibit “liquid-like” ionic conductivity values, while maintaining a quasi-solid or gel nature.^{16,17} Therefore, PAN-based gel-polymer electrolytes offer relatively higher ionic conductivities, especially at ambient temperature, and are thus suitable for fabricating more stable quasi-solid-state DSCs when they are prepared using non-volatile solvents.^{15,17–19}

1.2 Iodide ion (I⁻) conducting GPEs for DSCs

For the N719 dye-based DSCs, iodide ion (I⁻) conductors have been established as a better choice for preparing the redox electrolyte. One of the significant factors that influence the short circuit current density (J_{sc}) of a DSC is the iodide ion conductivity of the electrolyte. Hence, the efficiency of a solar cell is greatly dependent on the iodide ion conductivity.^{9,15} The iodide ions in the electrolyte contribute to the dye regeneration process also by providing an electron to the oxidized dye. It should be noteworthy to mention that the dye plays the role of light-harvesting in DSCs, thus higher dye regeneration kinetics are necessary to achieve higher photocurrents. Therefore, faster iodide ion transport is needed to enhance dye regeneration kinetics, which in turn enhances the light-harvesting efficiency of the cell. Therefore, in order to enhance iodide ion conductivity, the iodides with bulky cations such as tetrapropylammonium iodide (Pr₄N⁺I⁻), tetrabutylammonium iodide (Bu₄N⁺I⁻) and tetrahexylammonium iodide (Hex₄N⁺I⁻) have widely been investigated.^{9,15,17,20} Besides, several studies have suggested that the cation in the electrolyte has a significant positive impact on the short-circuit-current density (J_{sc}) and the electron dynamics at the electrolyte/photoelectrode interface.^{21–23}

Therefore, electrolyte cations make a major contribution to the enhancement of the efficiency of DSCs.

1.3 Recent advancements

In the recent literature, there have been several notable innovative approaches focused on enhancing the efficiency of DSCs by improving polymer electrolytes. Very recently, Pin Ma *et al.* reported a novel “soggy sand” type electrolyte by integrating ALOOH nanofibers into an ionic liquid electrolyte.²⁴ The authors managed to increase the conductivity four times by adding ALOOH nanofibers to an ionic liquid electrolyte. Accordingly, the DSC with ALOOH nanofibers in the electrolyte has shown an efficiency of 7.89%, which is a 29% increase compared to that with pure ionic liquid electrolyte.²⁴ In addition, the reported hybrid device prepared by amalgamation of properties of supercapacitors and DSCs gave a new insight into the research field of energy conversion and storage. Alberto Scalia *et al.* have designed a multipolymer electrolyte membrane separated by a cross-linked layer to combine the light-harvesting ability of DSCs and the storage ability of supercapacitors.²⁵ This novel hybrid photoelectrochemical device has exhibited a net conversion and storage efficiency of 3.72%, which is a remarkable value for a hybrid energy harvesting-storage device.

In another study, Federico Bella *et al.* reported an efficiency enhancement in aqueous electrolyte based solar cells by the treatment of TiCl₄ on TiO₂ electrodes.²⁶ TiCl₄ treatment has doubled the energy conversion efficiency values and furthermore, the study reported a higher stability over 16 days of aging the cells. The study has uncovered the importance of application of TiCl₄ treatment even for liquid electrolyte based DSCs.²⁶ Another important study reports an investigation on the nano-scale growth and crosslinking of a polymer electrolyte inside the nanostructured photoelectrode. In the study,²⁷ the electrochemical and photovoltaic performance dependence on the thickness and degree of penetration of the electrolyte has been investigated and thus, optimization of the amount of polymer, cell efficiency and stability have been managed. Importantly, the cell stability test conducted for 1000 h proved the higher stability offered by polymer electrolytes.²⁷

Very recently, Liu *et al.*²⁸ reported another new approach by introducing carbon nanotube (CNT) electrolytes intended for DSCs. The role of CNT in the electrolyte deviates from the role of conventional gelators. However, the authors managed to improve the efficiency from 8.15% to 8.70% as a result of the improvement of open-circuit voltage by addition of CNT.²⁸

Binary-counter ion effect. As reported recently, GPEs with a mixture or a combination of iodide salts have shown improved DSC performance compared to that of single salt electrolytes.^{18,19,29–32} The effect has been attributed to the dual role played by small and large cations to stimulate the photocurrent and photo-voltage. The method provides a way to improve DSC performance without degrading the mechanical properties of the electrolyte.

The bulky cations such as Pr₄N⁺, Bu₄N⁺ and Hex₄N⁺ are known to minimize the cationic conductivity and, in turn, improve the iodide ion conductivity in the electrolyte. Cations

with high charge density, such as Li^+ , Na^+ or K^+ , get absorbed into the TiO_2 electrode and consequently lead to improved photogeneration of electrons in the dye and improved diffusion dynamics at the dye–semiconductor interface.^{18,19,24}

In order to make use of both aforementioned mechanisms, it would be better to explore the combined effect of binary mixtures of iodide salts (one with a bulky cation and the other with a small alkali cation) in electrolytes. To investigate these binary cation effects in detail, we have studied the present system by choosing KI as the salt with small alkali and Hex_4NI as the salt with a bulky quaternary ammonium cation. This study aims at enhancing the efficiency of DSCs composed of PAN-based GPEs. For this purpose, the composition of a binary mixture of iodides KI and Hex_4NI is optimized in order to maximize the short circuit photocurrent density through enhanced iodide ion conductivity. To our knowledge, only a few studies are reported in the literature on utilizing this type of binary iodide salt mixture on the efficiency enhancement in quasi-solid-state DSCs, and this is the first report on GPEs made with a KI and Hex_4NI mixed iodide salt system intended to enhance efficiency in DSCs. In this work 4-*tert*butylpyridine (4TBP) and 1-butyl-3-methylimidazolium iodide (BMII) have been used as additives to obtain a better DSC performance³³ and hence to get an impressively higher DSC performance.

2. Experimental

2.1 Preparation of electrolyte

Polyacrylonitrile (PAN), tetrahexylammonium iodide, KI, iodine (I_2), PC and EC (all with purity greater than 98%) purchased from Sigma-Aldrich were used as starting materials. PAN, KI, and Hex_4NI were vacuum dried at 60 °C for 24 h prior to use. Weights of EC (1.6604 g), PC (1.5404 g), 4TBP (0.0868 g) and BMII (0.0504 g) were kept unchanged in all the electrolyte samples. The relative weights of KI and Hex_4NI were varied, keeping their total weight constant at 0.37 g. The weight of iodine (I_2) was 0.384 g, which is about one-tenth of the total mole amount of the iodide from the two salts. Appropriately weighed quantities of EC, PC, 4TBP, BMII, KI and Hex_4NI were mixed under continuous stirring at room temperature for ~2 h until the entire amount of salts dissolved. After adding 0.4 g of PAN, the mixture was stirred again for about 30 min. Then the mixture was heated to about 80 °C together with continued stirring for about 15 min more. The resulting mixture was allowed to cool down to ambient temperature. Finally, I_2 chips (384 mg) were added and again continuously stirred overnight in a closed bottle to obtain a homogeneous gel-electrolyte. This procedure was repeated for all the electrolyte compositions given in Table 1. Three electrolyte samples were prepared and tested for each composition and the samples with most reproducible results were selected for the analysis.

2.2 Electrolyte characterization

Ionic conductivities of the five electrolyte samples were extracted from the complex impedance spectroscopic data measured using

Table 1 Weights and weight fractions (percentages) of KI and Hex_4NI used to prepare the PAN-based gel-polymer electrolytes

Electrolyte	KI wt%	Hex_4NI wt%	KI/mg	Hex_4NI /mg
A	0	100	0	370.0
B	25	75	92.7	277.5
C	50	50	185.0	185.0
D	75	25	277.5	92.7
E	100	0	370.0	0.0

a Metrohm Autolab (PGSTAT 128N, Netherlands) impedance analyzer in the frequency range 1 Hz–1 MHz. For this purpose, the electrolytes were sandwiched between two polished stainless steel (SS) electrodes with configuration SS/electrolyte/SS. The temperature of the electrolyte sample was varied from ~75 °C to room temperature in steps of ~5 °C. The temperature of the sample was allowed to stabilize for ~15 min for each measurement. The measurements were taken on the cooling runs (from 75 °C to 23 °C). The bulk DC conductivity and complex AC conductivity values of the electrolytes were calculated from the impedance data. The glass transition temperatures of the electrolytes were estimated by using a Mettler Toledo DSC 30 differential scanning calorimeter. The temperature scanning was conducted between –120 °C and 120 under ± 10 °C min^{-1} heating/cooling rate.

2.3 TiO_2 electrode preparation

Two successive layers of TiO_2 were deposited on the FTO conducting glass substrate in order to prepare the photoanode. The mixture for the 1st layer was prepared by grinding 0.5 g of P90, TiO_2 nanoparticles (Evonik-Degussa) with 2 ml of 0.1 M nitric acid, in a mortar for ~30 min. The resulting slurry was coated on a well-cleaned FTO glass substrate by spinning at a speed of 2300 rpm for 60 s. During the spin-coating, a part of the glass plate was covered with an adhesive tape to prevent coating TiO_2 on the area needed for electrical contacts. After air-drying for 30 min, the TiO_2 coated electrodes were sintered at 450 °C for ~30 min and subsequently allowed to cool down gradually to room temperature (-0.5 °C min^{-1}). Subsequently, the second layer of TiO_2 was coated on the top of the first layer using P25 TiO_2 nanoparticles (Evonik-Degussa). For the preparation of this layer, 0.5 g of TiO_2 powder was ground well for ~30 min with 2 ml of 0.1 M nitric acid in a mortar. Subsequently, 0.1 g of Carbowax and a few drops of Triton X 100 (surfactant) were added and the mixing continued for another few minutes. This colloidal suspension was cast using the doctor blade method followed by sintering at 450 °C for 30 min to obtain a porous layer of TiO_2 nanoparticles. Finally, the dye sensitization process was carried out by immersing the TiO_2 coated glass plates in a saturated solution of ruthenium N719 (Solaronix SA) in ethanol. The temperature of the dye solution is 60 °C at the dipping moment, and the sample is then kept soaking in it for ~24 h at the room temperature.

2.4 Solar cell fabrication and characterization

Gel-polymer electrolyte-based DSCs, with the configuration FTO/ TiO_2 /dye/electrolyte/Pt/FTO were assembled by sandwiching

the electrolyte film between the dye-sensitized TiO₂ electrode and the Pt counter electrode (Pt-coated glass). The photo-current voltage (*I*-*V*) characteristics of the solar cells were measured under the irradiation of 1000 W m⁻² (1.5 AM) with a solar simulator (ABET technologies) using a 0.19 mm² aperture. Current-voltage data were measured and recorded using a Metrohm Autolab (PGSTAT 128N) with Nova software at the scan rate of 0.1 V s⁻¹. Three cells of each composition were tested and the most stable was selected for the analysis.

3. Results and discussion

3.1 DC conductivity

The temperature dependence of ionic conductivity of the electrolytes is illustrated in Fig. 1. In order to calculate these ionic conductivities, the bulk DC resistances of the electrolytes were extracted from Nyquist plots. As an example, the Nyquist plots of sample A taken at different temperatures between 23 °C and 70 °C are shown in Fig. 2. All the other samples (B to E) also exhibited similar curves (not shown). The DC resistance values obtained were used to estimate the ionic conductivity of the electrolytes shown in Fig. 1.

The trend seen in Fig. 1 is non-Arrhenius. The ionic conductivity of this gel electrolyte increases with the increased amount of KI and the decreased amount of Hex₄NI. This behavior is expected since the contribution to the conductivity from ionic mobility of the bulky cation Hex⁺ is very small compared to that of small size cation K⁺, as inferred from the transference number studies given for the analogous systems.^{30,31} As shown in Fig. 1, the highest conductivity is exhibited by the electrolyte, which has 100% KI and 0% Hex₄NI mass fractions (sample E). The room temperature conductivity of this electrolyte sample, E, is as high as 3.74 mS cm⁻¹. The conductivities of this sample at 50 and 70 °C are 6.07

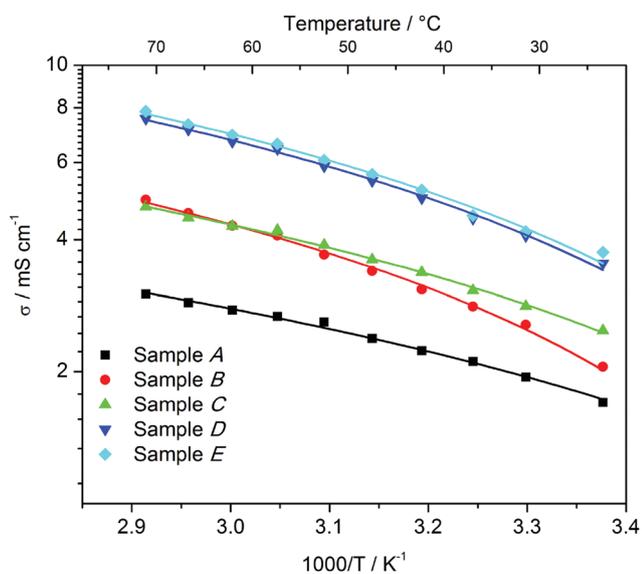


Fig. 1 Conductivity Arrhenius plots of the PAN-based GPEs prepared with different amounts of KI and Hex₄NI salts.

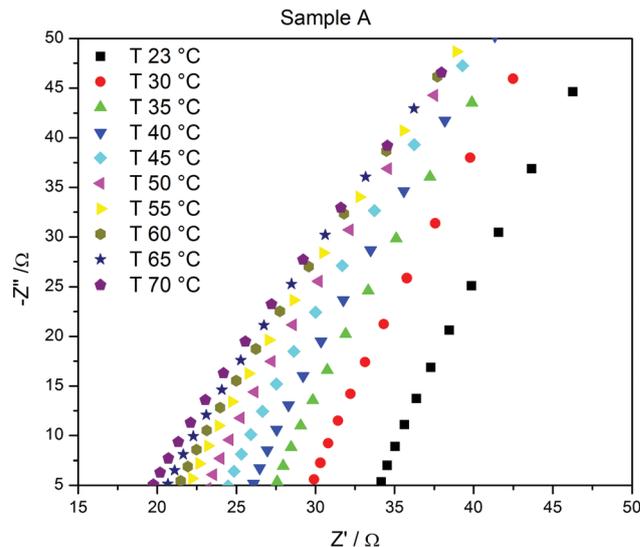


Fig. 2 Nyquist plots for electrolyte sample A (containing 100% Hex₄NI) taken at different temperatures from 23 to 70 °C.

and 7.86 mS cm⁻¹ respectively. It is also seen that the conductivities of the electrolyte samples D and E, in the studied temperature range, are close to each other. The recorded conductivities of all the electrolytes are sufficiently high enough to prepare high-efficiency quasi-solid-state DSCs. However, it should be noted that the ionic conductivities of all these electrolyte samples consist of contributions from both cations and anions. Samples D and E exhibit higher ionic conductivities than that of other samples, evidently due to the contribution of a higher concentration of small-sized K⁺ ions with a higher mobility in these samples. However, it will be the contribution from iodide anions (I⁻) which would eventually determine the short circuit photocurrent density as already reported for several DSC systems.^{18,19,30} Due to this factor, the electrolytes that give higher iodide ion conductivity are more suitable for fabricating highly efficient DSCs. In this context, previous studies have demonstrated in detail the advantages of using a combination of iodide salts containing small and large cations instead of a single iodide salt electrolytes in order to enhance the performance of quasi-solid-state DSCs.^{19,30}

Since Fig. 1 is non-Arrhenius, $\ln(\sigma T^{1/2})$ is plotted as a function of $(T - T_g)$ (in Fig. 3) in order to understand the temperature dependence of the conductivity. As clearly shown in Fig. 3, the conductivity variation with temperature exhibits the VTF (Vogel-Tammann-Fulcher) type behavior.^{34,35} The measured glass transition temperatures (T_g) of the samples are about 100 °C. These measured glass transition temperatures were used as T_0 for the curve fitting. The appropriateness of this selection of T_g as T_0 is confirmed by the better fitting shown in Fig. 3. The pseudo-activation energy and pre-exponential factors were calculated by fitting the data to the VTF eqn (1) and tabulated in Table 2.

$$\sigma(T) = AT^{-1/2} \exp\left[\frac{-E_a}{k_B(T - T_0)}\right] \quad (1)$$

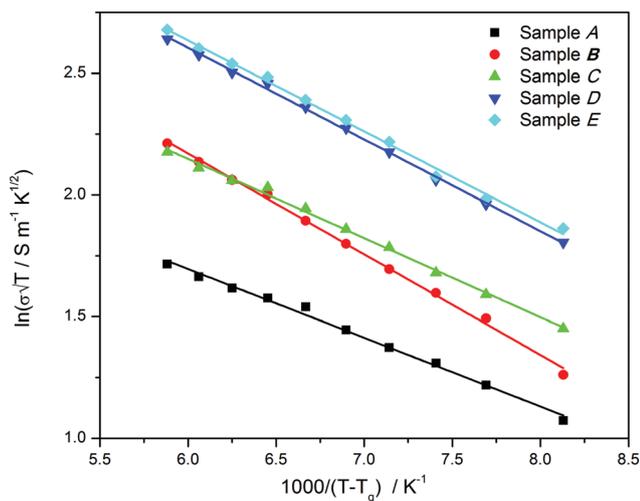


Fig. 3 $\ln(\sigma T^{1/2})$ versus $(T - T_g)$ plots of the PAN-based GPEs prepared with different amounts of KI and Hex₄NI salts.

Table 2 The activation energy, E_a , and pre-exponential factor, A , for electrolytes with different mass fractions of KI and Hex₄NI salts given in Table 1

Sample	$A/S \text{ m}^{-1} \text{ K}^{1/2}$	E_a/eV
A	29.67	0.024
B	104.97	0.035
C	60.22	0.028
D	129.49	0.032
E	130.96	0.032

The activation energy (E_a) and pre-exponential factor (A) increase with increasing mass fraction of KI except for sample B. Sample B has shown a slightly lower activation energy, which can be attributed to higher disorder imposed by the addition of small amounts of KI to the single salt system. Added disorder can improve the amorphousness of the electrolyte leading to enhancement of the ionic conductivity.³⁵

3.2 Complex AC conductivity

In general, the complex conductivity in an electrolyte is affected by different types of polarization.³⁶ The electrolytes studied in this work can undergo different polarizations such as electrode polarization, dipole polarization, ionic polarization, as well as electronic polarization due to their complex nature. Besides, dielectric relaxations and the dynamics of ionic species and dipoles can modify the ionic conduction as well as the dielectric behavior of the electrolyte. Therefore, the real and the imaginary parts of the AC conductivity of electrolytes are investigated as a function of frequency at different temperatures.

Variations of the real part of the AC conductivities ($\sigma_{(\omega)'}^r$) of the series of electrolytes (from A–E) are shown in Fig. 4, as a function of the frequency at different temperatures. Apparently, all the AC conductivity curves reach plateau values at low frequencies as well as at high frequencies. The high-frequency plateaus in Fig. 4 can be attributed to reaching the conductivity to its DC limit. These high-frequency values are comparable

with the DC conductivities calculated using Nyquist plots. In order to analyze and compare these high-frequency plateau values of AC conductivity (σ') with the DC conductivity, the values at 10^5 Hz are given in Table 3. These high-frequency plateau values increase with increasing temperature for all the samples, which can lead to increased ion transport kinetics with increasing temperature. They are comparable with the conductivities given in Fig. 1.

As seen from Fig. 4(A)–(E), with decreasing frequency, the AC conductivity drops exponentially, and the trend can be attributed to the limitations in the change of polarization with frequency. Therefore, a strong frequency and temperature dependence of $\sigma_{(\omega)'}$ can be observed in all the samples. In order to understand the exponential drop of σ' at low frequencies ($1 \text{ Hz} \leq f \leq 100 \text{ Hz}$), σ' is plotted in logarithmic scale and shown in the insets of Fig. 4(A)–(E). Though it appears that σ' reaches a plateau at low frequencies, the actual trend at low frequency is an exponential drop with decreasing frequencies as seen from the insets of Fig. 4(A)–(E). This exponential drop can be related to electrode polarization effects,^{37,38} which in general increase with decreasing frequency. Simply at low frequencies, more charges accumulate at the electrode–electrolyte interface resulting in a decrease in the number of mobile ions in the bulk. This reduction of charge carrier concentration in the bulk reduces the conductivity, as seen in Fig. 4. However, owing to the fast charge transport dynamics of this electrolyte, the high-frequency dispersive part is not visible in the measured frequency range.^{37,38} In order to understand the polarization effects governed by ionic motion in the bulk, the low-frequency part of the $\sigma_{(\omega)'}$ is fitted to the equation:

$$\sigma_{(\omega)'} = A\omega^n \quad (2)$$

where ω is the angular frequency of the applied AC signal and n is a factor which depends on the polarization. The parameter n is calculated for all the samples and tabulated in Table 4, which can possibly be used as a measure of interfacial polarization.

The imaginary part of the complex conductivity ($\sigma_{(\omega)''}$) is also plotted against frequency for each sample at different temperatures and are shown in Fig. 5. All the curves show a similar trend, but move upward with increasing temperature. In general, the imaginary part, σ'' , is resulted by the contribution of capacitive effects of the cell prepared by sandwiching an electrolyte between two SS blocking electrodes. The imaginary part of the complex conductivity peak values seen at about 10 kHz can be due to the relaxation of interfacial charge transport which more or less increases with increasing mass fraction of KI. The temperature dependence of the peak values of σ'' is also shown in Fig. 5. The exhibited relatively larger peaks by sample B at higher temperatures (Fig. 5), may be a consequence of the lower conductivity activation energy (Table 2) of the sample.

The tangent of the phase angle $\left(\tan \phi = -\frac{Z''}{Z'}\right)$ of the impedance is also plotted against the frequency for each sample at various temperatures and is shown in Fig. 6(A–E).

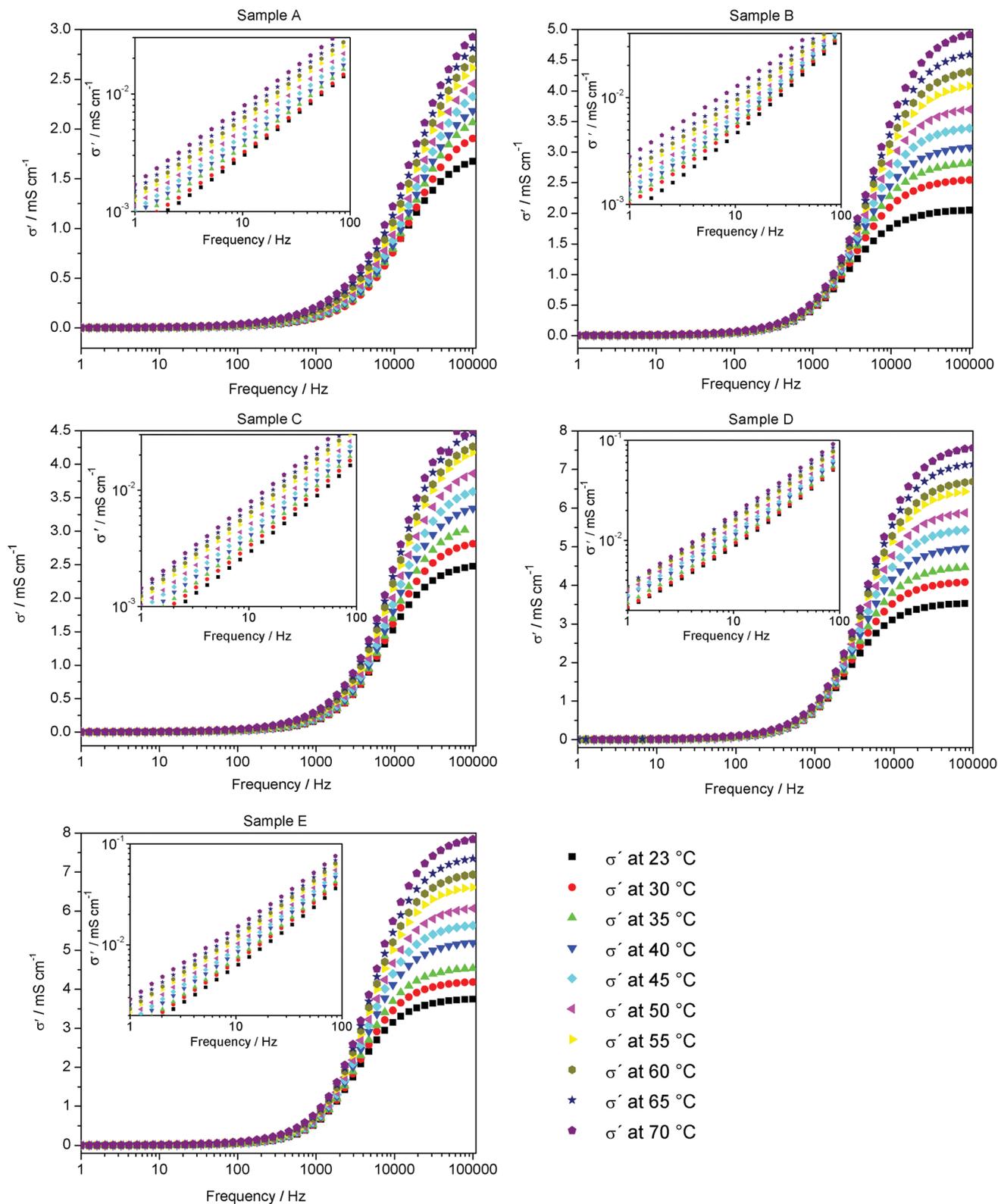


Fig. 4 Frequency dependence of the real part of the AC conductivity ($\sigma'_{(\omega)}$) in electrolyte samples, with different amounts of KI and Hex₄NI, at different temperatures. The inset of each curve shows the low-frequency part of $\sigma'_{(\omega)}$.

The peak values of $\tan\phi$ are also shown in Fig. 6. These relaxation times (time constant) correspond to peak values,

which are related to electrode polarization. The peak height is increasing with the increasing mass fraction of KI except for

Table 3 AC conductivity ($\sigma_{(\omega)}$) values at 10^5 Hz in mS cm^{-1} for the electrolytes given in Table 1 at different temperatures

Sample	23/°C	30/°C	40/°C	50/°C	60/°C	70/°C
A	1.68	1.91	2.18	2.46	2.70	2.93
B	2.05	2.54	3.08	3.70	4.31	4.92
C	2.47	2.81	3.34	3.65	4.26	4.50
D	3.53	4.08	4.97	5.88	6.69	7.56
E	3.74	4.18	5.19	6.07	6.94	7.84

Table 4 n values in eqn (2) for the electrolytes given in Table 1 at different temperatures

Sample	23/°C	30/°C	40/°C	50/°C	60/°C	70/°C
A	0.75	0.75	0.73	0.72	0.71	0.70
B	0.78	0.79	0.79	0.78	0.76	0.74
C	0.82	0.82	0.81	0.80	0.79	0.77
D	0.78	0.79	0.78	0.78	0.76	0.76
E	0.81	0.81	0.81	0.81	0.80	0.78

sample B. The relatively higher peak values shown by sample B can be attributed to the lower conductivity activation energy. As seen in Fig. 6, the time constant related to electrode polarization is decreasing with increasing temperature as a result of faster charge transport dynamics at higher temperatures.

3.3 DSC characterization

The influence of cations (counterions) on the performance of gel polymer electrolyte based DSCs can be investigated by separating their contribution into two categories. (1) The effect of the nature of cations in the electrolyte to modify the conductivity in the electrolyte. (2) Cations in the electrolyte, depending on their size and charge density, get adsorbed onto or intercalate into the nanostructured TiO_2 electrode and modify the conduction band edge of the TiO_2 film.^{22,30,39}

The 1st effect can be understood by studying the ionic conductivity of the electrolyte as we did in this work by analyzing AC and DC conductivities. The charge transport process of a DSC is governed by the conductivity in the electrolyte since the series resistance of a functioning DSC is dominantly contributed by the resistance of the electrolyte. Therefore, as generally accepted, the photocurrent and the short circuit current density of a DSC are governed by the conductivity in the electrolyte, or in particular, by Γ/Γ^{3-} conductivity. The conductivity in polymer electrolytes (as shown in Fig. 1), drastically depends on the nature of the cation, as previously described in detail,²² due to ion polymer interactions changing the chemical and physical surroundings of mobile ionic species. The 2nd effect can be understood by studying the shift of conduction band edge as well as influence to alter the Helmholtz double layer at the electrolyte photoelectrode interface, as previously explained in detail.^{30,40,41} Mainly, the V_{oc} of the cell is governed by this effect.³⁹ When the cell is at the open circuit, the electrical current does not flow through the external circuit, and the V_{oc} is the shift of Fermi level of the photoelectrode relative to the redox level of the electrolyte, at the equilibrium. The shift of the Fermi level is controlled by the number of photo-generated electrons in the

conduction band of a functioning cell, at equilibrium.²² High charge density cations, such as Li^+ , in the electrolyte, get adsorbed into the TiO_2 structure and make a positive shift of the conduction band, thereby facilitating the photoelectron generation and enhancing the photocurrent. This is also associated with a drop in the V_{oc} as it hinders the relative shift of the conduction band as well as the Fermi level resulting in a drop of V_{oc} .

A series of DSCs were assembled using KI and Hex_4NI based electrolyte samples prepared according to the compositions given in Table 1. Photocurrent density and power density *versus* cell potential (J - V) curves were used to calculate the short circuit current density (J_{sc}), the open-circuit voltage (V_{oc}) and the energy conversion efficiency. The variation of V_{oc} , J_{sc} and the energy conversion efficiency of the electrolytes with the increasing amount of KI and decreasing amount of Hex_4NI are shown in Fig. 7 and 8.

The present work also clearly demonstrates the mixed cation effect on the performance of DSCs based on GPEs.^{18,19,24} The ionic conductivity of this electrolyte increases with the increasing amount of the KI and decreasing amount of the Hex_4NI , as shown in Fig. 1. However, as seen in Fig. 7 and 8, the solar cell parameters do not follow the trend of ionic conductivity. According to Fig. 7, the highest V_{oc} is given by the cell containing electrolyte sample C with 50% KI and 50% Hex_4NI . Higher V_{oc} values are expected from the electrolytes with larger cations,^{22,31} and accordingly the cell with electrolyte sample A should exhibit the highest V_{oc} . Conversely, the ionic conductivity, which is also essential for the higher performance of a DSC, decreases with the increasing amount of the larger cationic salt Hex_4NI . As a result of the above mentioned two competing effects, the highest V_{oc} of 796 mV is exhibited by the cell containing electrolyte sample C.

The photocurrent density of a DSC depends on the ionic conductivity of the electrolyte, in particular, the iodide ion conductivity. In addition, the iodide ion conductivity drives the charge injection at the photoelectrode/electrolyte interface by improving the regeneration kinetics of the dye sensitizer. Furthermore, the cations in the electrolyte can govern the flat-band potentials of TiO_2 due to intercalation and adsorption of cations to the photo-electrode. In general, J_{sc} in this type of DSC depends primarily on the anionic conductivity in the electrolyte. The highest J_{sc} , as shown in Fig. 8, is given by the cell with the electrolyte sample D, which contains KI (75 wt%) and Hex_4NI (25 wt%). Though the single salt system (sample E with 100 wt% KI) exhibits a higher ionic conductivity than that of sample D (mixed salt system), the mixed cation effect has contributed to give the highest J_{sc} for the cell with electrolyte D. Moreover, in sample E, a significant contribution to the total ionic conductivity comes from the K^+ ion conductivity as well, which does not directly contribute to J_{sc} . The incorporation of 25 wt% of Hex_4NI (a salt with a large cation) can shift flat band potentials to more towards the negative potential and thus can increase the charge injection rates contributing to J_{sc} enhancement. As a result, the highest J_{sc} of 13.8 mA cm^{-2} is shown by the DSC with electrolyte sample D.

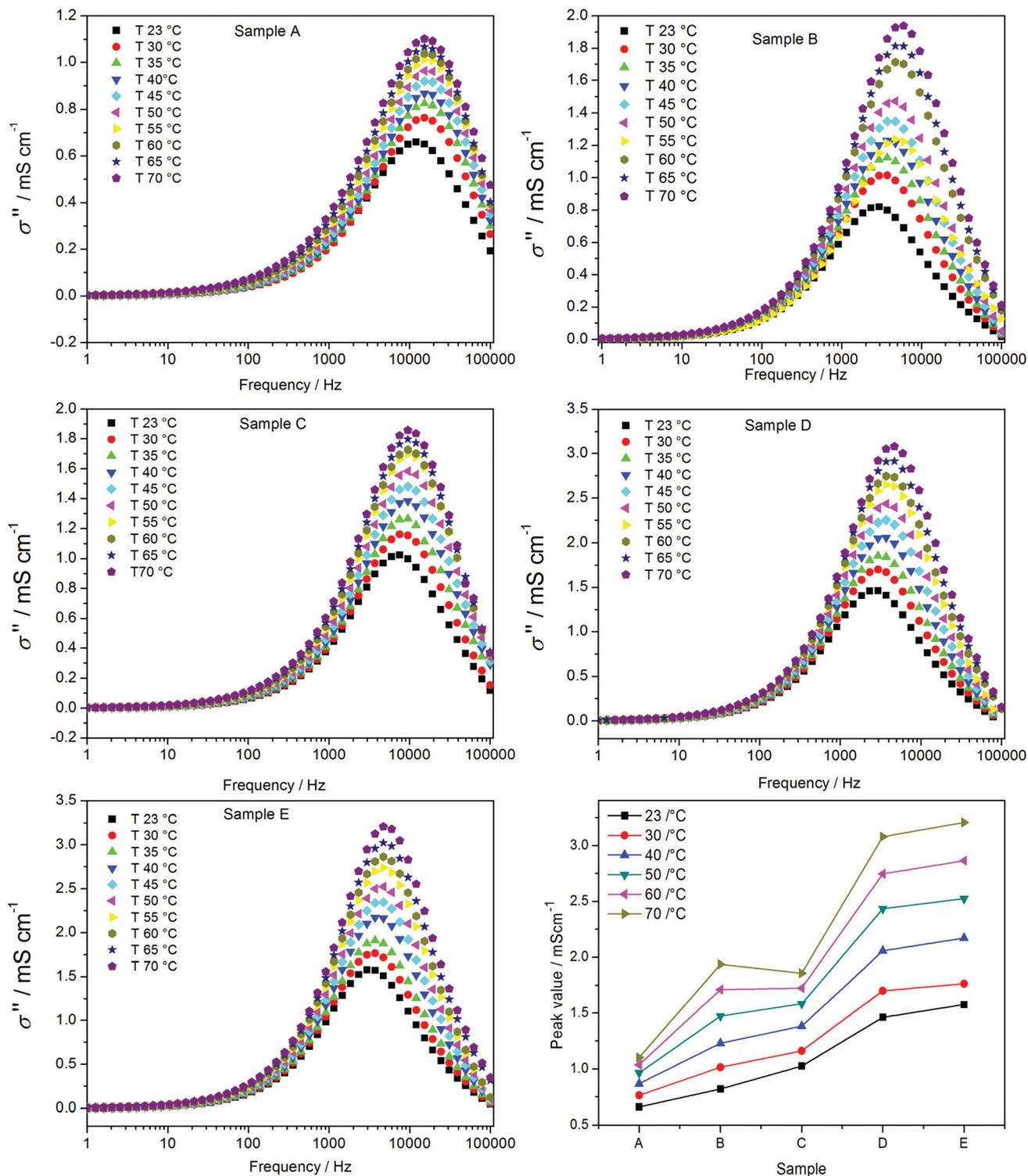


Fig. 5 The imaginary part of the AC conductivity (σ'') isotherms of electrolyte samples as a function of frequency. The bottom curve at the right shows the peak values of σ'' of the samples at different temperatures.

The energy conversion efficiencies of the DSCs prepared are shown in Fig. 8. All the cells studied in this work have shown efficiencies of over 5%. Each and every cell prepared in this study (including three cells prepared with each composition) exhibited efficiencies above 5% and the photocurrent did not

show any sign of degradation within the continued irradiation of about one hour. Highlighting the mixed salt effect, the cells with mixed salts have shown efficiencies greater than 6%. Consequently, an impressively high efficiency of 7.36% is shown by the quasi-solid-state DSC prepared with the electrolyte sample D.

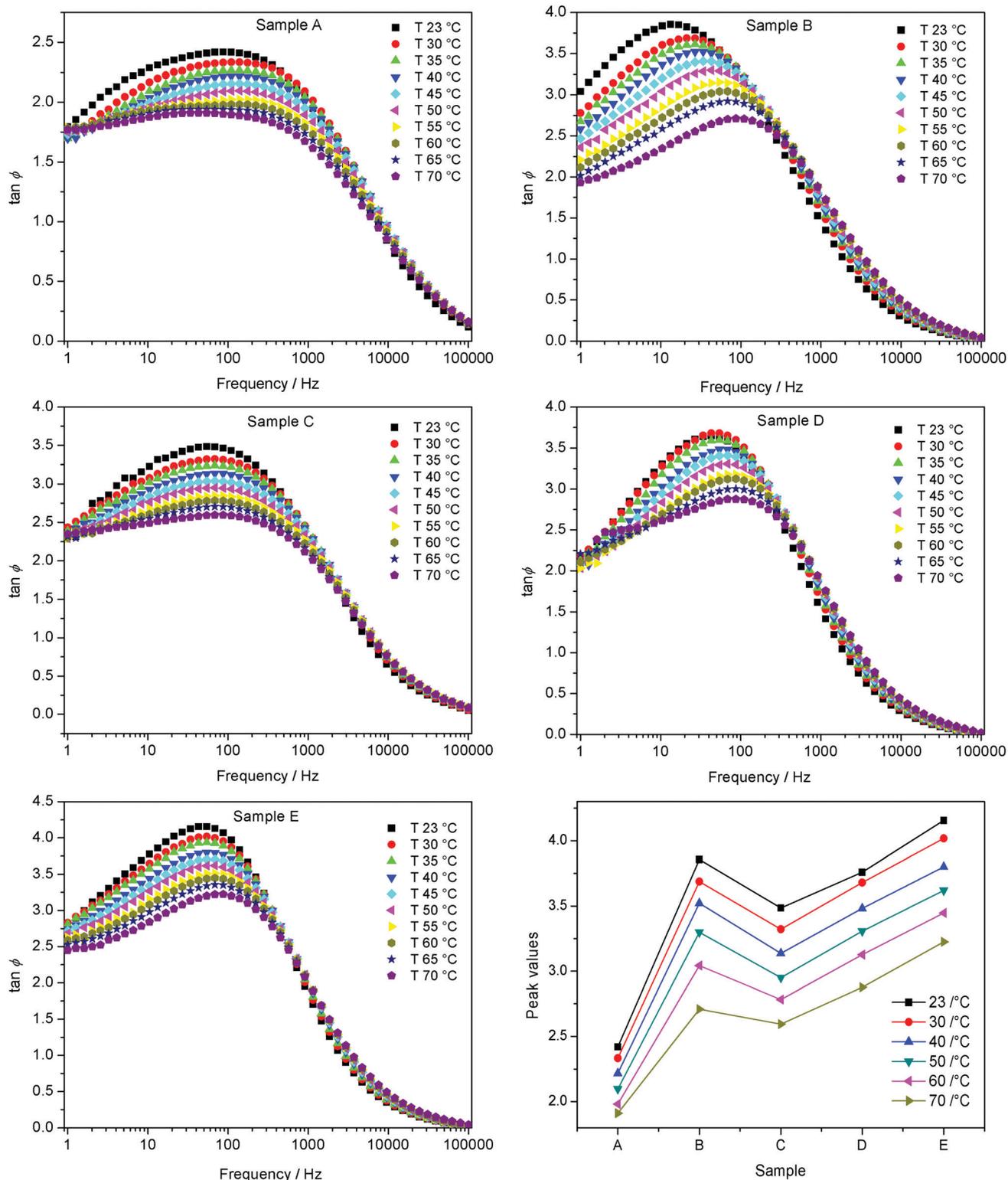


Fig. 6 The tangent of the phase angle ($\tan \phi = -\frac{Z''}{Z'}$) of the impedance against the frequency for electrolyte samples at various temperatures. The bottom curve at the right shows the peak values of the samples at different temperatures.

This study suggests that the salt combination of KI and Hex_4NI is a novel iodide salt mixture suitable to fabricate highly efficient DSCs. Furthermore, since we did not include any volatile solvents, such as

acetonitrile, acetone, ethanol, *etc.* in the electrolyte, the fabricated DSC is an environmentally friendly, stable device with a significantly high energy conversion efficiency of 7.36%.

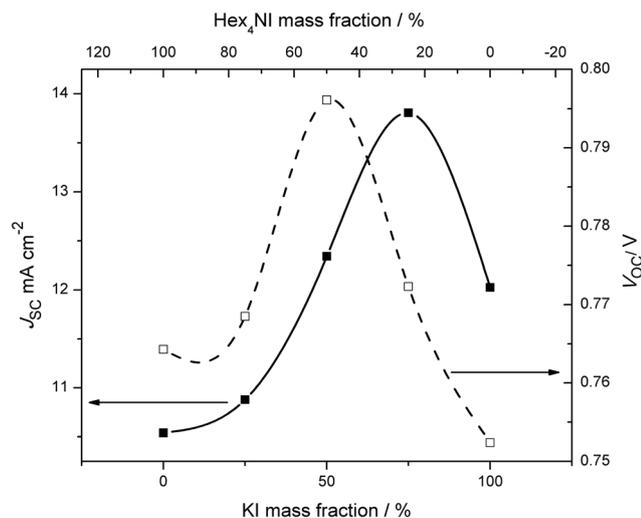


Fig. 7 Variation of V_{oc} and J_{sc} in DSCs as a function of KI and Hex₄NI contents in the electrolyte.

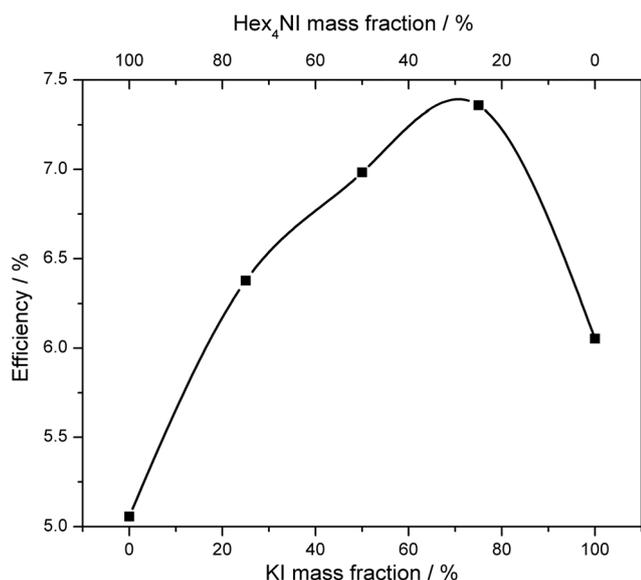


Fig. 8 Variation of the energy conversion efficiency in DSCs as a function of the KI and Hex₄NI composition ratio in the electrolyte.

4. Conclusions

A new set of GPEs based on the PAN polymer host, which is suitable to fabricate highly efficient quasi-solid-state DSCs harnessing the mixed cation effect, were investigated. The new GPEs are composed of PC and EC co-solvents, tetrahexylammonium iodide (Hex₄NI) and KI salts and 4-*tert*-butylpyridine and 1-butyl-3-methylimidazolium iodide performance enhancers. The analysis of ionic conductivity in electrolytes reveals that the temperature dependence of the electrolyte exhibits VTF (non-Arrhenius) behavior. The ionic conductivity in the electrolyte increases with the increasing mass fraction of KI (decrease of Hex₄NI). The highest conductivities at all the temperatures are given for sample E with 100 wt% KI and it shows values of

3.74, 6.07 and 7.86 mS cm⁻¹ at 23, 50 and 70 °C, respectively. The frequency dependence of the real and imaginary parts of the AC conductivity is analyzed in order to understand polarization effects on electrical/dielectric properties. The real part of the AC conductivity increases with increasing temperature as well as increasing frequency as a result of an increase in ion transport dynamics. Peak values of the imaginary part of the AC conductivity are visible at about 10 kHz due to charge transport relaxation.

A set of DSCs assembled using N719 dye-sensitized TiO₂ electrodes and the new electrolyte series showed efficiencies higher than 5%. Highlighting the mixed cation effect, the cells with mixed iodide salts show efficiencies greater than 6%. Consequently, an impressively high energy conversion efficiency of 7.36% is achieved by the quasi-solid-state DSC prepared with an electrolyte containing 75% KI and 25% Hex₄NI. This study suggests that the salt combination of KI and Hex₄NI provides a suitable iodide salt mixture for the fabrication of high-efficiency DSCs.

Conflicts of interest

There are no conflicts to declare.

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