Electrochemical Characterization of 1-Ethyl-3-methylimidazolium Thiocyanate and Measurement of Triiodide Diffusion Coefficients in Blends of two Ionic Liquids

*M. Zistler [1], C. Schreiner [1], P. Wachter [1], P. Wasserscheid [2], D. Gerhard [2], and H. J. Gores [1, *]*

[1]Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-93053 Regensburg, Germany
[2]Institut für Chemische Reaktionstechnik, Friedrich-Alexander Universität, D-91058 Erlangen-Nürnberg, Germany
[*]E-mail: w.heitzer_h.j.gores@t-online.de

According to literature, binary mixtures of ionic liquids (ILs) such as 1-methyl-3-propylimidazolium iodide (MPII) as an iodide source and another IL of low viscosity such as 1-ethyl-3-methylimidazolium thiocyanate (EMISCN) may be used to increase the diffusion coefficients of redox-active species (I^-/I_3^-). As dye-sensitized solar cells (DSCs) are diffusion limited a better performance may result with blends when compared to cells based on MPII alone. In order to learn more about EMISCN and its blends with MPII, we electrochemically characterized this IL and measured diffusion coefficients of triiodide in binary mixtures containing EMISCN by polarization and impedance studies at thin layer cells with a distance between Pt-electrodes of about 30 to 40 µm. The electrochemical windows of the used ILs were measured by cyclic voltammetry (CV) and compared to those of other ILs, recently investigated by us.

1. INTRODUCTION

In 1991 O'Regan and Grätzel developed the dye-sensitized solar cell (DSC) as a low-cost and highly efficient alternative to conventional photovoltaic cells. [2] This cell is a regenerative photoelectrochemical solar cell based on the redox-couple (I^-/I_3^-). At present an efficiency of more than 10% can be obtained with DSCs using electrolytes based on volatile organic solvents. [3] But there are some drawbacks in the use of volatile organic solvents concerning the sealing of the cell and its long term stability. [4,5] A good alternative to organic solvents are ionic liquids (ILs), due to their

properties, such as non-volatility, non-flammability, and high ionic conductivity. [6] Among these materials for DSCs most attention was paid to ILs with 1,3-dialkylimidazolium cations, [7] especially to 1-methyl-3-propylimidazolium iodide (MPII), as an iodide source in the electrolyte. However, due to the high viscosity of MPII (695 cP at 25 °C) [8], binary IL electrolytes, using MPII and low viscous ILs, such as 1-ethyl-3-methylimidazolium dicyanamide (EMIDCA) [9] or 1-ethyl-3-methyl-imidazolium thiocyanate (EMISCN 21 cP at 25 °C) [1,10] were studied in DSCs and good cell performances were reported.

2. EXPERIMENTAL PART

2.1. Chemicals and purification

1-Methylimidazole (99%) and 1-iodopropane (99%) were purchased from Aldrich Corporation and distilled prior to use. MPII was synthesized by reacting 1-iodopropane with 1-methylimidazole in dry dichloromethane at 40 °C. EMISCN (Iolitec, Freiburg, Germany) with a purity of $\geq$ 99% and MPII used in electrochemical experiments were dried in high vacuum (HV 10^{-3} Pa), yielding water contents of 31 ppm (EMISCN) and 57 ppm (MPII), respectively, both determined by Karl-Fischer titration. The purity of the synthesized MPII ($\geq$ 99%) was determined by NMR.

Acetonitrile (AN) and tetraethylammonium tetrafluoroborate (TEABF$_4$) used in CV measurements were purchased from Merck, both grade Selectipur (battery grade). The water content of the AN was 36 ppm. The iodine used for the diffusion measurements was obtained from Riedel-de Haën, purity $\geq$ 99.8%.

2.2. Electrochemical experiments

Diffusion measurements were performed at a thin layer cell, for details see elsewhere. [11] The two electrodes of the cell were made of platinized transparent conducting oxide (TCO, SnO$_2$:F, TEC-8 from Pilkington)-coated glass. Platinization has been done by sputtering, resulting in a mass-thickness of platinum layers of 3 to 4 nm. The electrodes with a surface area of 2.5 cm^2 showed a distance of about 30 to 40 µm, using glass frit as a spacer and sealant. Due to the large variation of the electrode distance l, this distance had to be determined for every cell used in diffusion measurements. Two identical electrodes have been mounted onto each other and sealed in a fusing step at approx. 600 °C.

The electrolyte was injected into the cells after sealing through tiny filling holes. The exact distance between the electrodes was determined indirectly by calibration via diffusion coefficient measurements and directly by using a digital micrometer, accuracy about 1 µm.

Calibration was performed with an aqueous solution of 0.025 mol/L K$_3$[Fe(CN)$_6$], 0.25 mol/L K$_4$Fe(CN)$_6$, 0.5 mol/L KCl; the distance could be calculated with the measured limiting current density and the diffusion coefficient of the hexacyanoferrate ion given in literature [12], D([Fe(CN)$_6$]$^{3-}$) = 7.17×10^{-6} cm^{2}s^{-1}.

Despite the fact that both methods yielded nearly the same values and the same errors from four measurements in test runs to state the precision of both methods, yielding $l = 38 \pm 4$ µm for

mechanical determinations and $l = 37 \pm 4$ μm for calibrations at one cell, respectively, only calibration can be recommended, as the mechanical measurement is much more difficult to handle. In addition, if the electrodes are not completely parallel and planar, this effect is taken into account when the distance is determined by electrochemical calibration. Therefore the electrode distance for every cell used for diffusion measurements reported below was determined by calibration.

Thin layer cells were filled with electrolyte in a glove-box under argon atmosphere at water and oxygen contents of a few ppm and sealed gas tight with a Surlyn foil (Dupont). The diffusion measurements were carried out outside of the glove box at a temperature of 25 ± 0.02 °C in a thermostat (LAUDA, Lauda-Königshofen, Germany, RK 8 KP).

Voltage windows were measured by cyclic voltammetry with a three electrode setup. The working electrode (WE) and the counter electrode (CE) were Pt electrodes; the reference electrode (RE) was prepared according to Izutzu [13] i. e. a non-aqueous Ag/Ag^+-Kryptofix electrode slightly modified by us to reduce the diffusion potential. It was prepared by adding 25 μL of a solution containing 0.205 mol/L $AgNO_3$ and 0.410 mol/L Kryptofix 22 (Merck, for synthesis) in acetonitrile to 1 mL of the base electrolyte (AN, $TEABF_4$, for the concentration see below) and filling this blend into a glass vessel (manufacturer: Bioanalytical Systems Inc. USA (BAS)), equipped with a Vycor® tip (BAS), introducing an Ag-wire (BAS) into this solution and closing the glass vessel. All operations were performed in a glove box. As nearly the same electrolyte concentrations are used in the reference electrode and in the studied solution, only negligible diffusion potential results.

Polarization measurements and determination of voltage windows were carried out with an IM6, controlled by the Thales Software from Zahner, Kronach, Germany. Impedance spectroscopy was performed with a Solartron 1260 Impedance/Gain-Phase Analyzer (StandAloneMode) from Solartron Analytical, Farnborough, United Kingdom, controlled by the ZPlot-Software from Scribner Associates Inc., Southern Pines, USA. For the analysis of the impedance spectra the ZView-Software was used, also from Scribner Associates.

3. RESULTS AND DISCUSSION

3.1. Diffusion Coefficient Measurements

Two electrolyte compositions were prepared to determine the I_3^--diffusion coefficient: electrolyte A (0.04 mol/kg I_2 in the mixture of MPII and EMISCN (weight ratio 0.11:1) and electrolyte B (0.050 mol/L I_2 in a mixture of MPII and EMISCN (weight ratio 1:1)). The density of electrolyte B was determined with a precision densitometer (DMA 60 / DMA 602, Paar, Graz, Austria) to calculate the exact molar concentrations. Both electrolytes weren't stable. A solid precipitate was observed after one day for electrolyte A and after four weeks for electrolyte B. So we could only determine the I_3^--diffusion coefficient in the electrolyte B. The density of electrolyte B at 25 °C was 1.304 kg/L.

The diffusion coefficient was measured by polarization and impedance studies at thin layer cells. Both methods are suitable for a determination of I_3^--diffusion coefficient in ionic liquid

electrolytes, since the methods were tested and compared to other diffusion measurement methods based on electrochemical measurements at microelectrodes. [14] Although the determination of triiodide diffusion in ILs based on microelectrode techniques yields values with high precision [15], diffusion investigation based on measurements at thin layer cell were chosen, due to the small amount of electrolyte needed by this method.

Due to the large excess of iodide, triiodide is the diffusion-limiting species and therefore its diffusion coefficient can be determined.

Figure 1 shows a typical polarization measurement for electrolyte B. The diffusion-limiting current density was determined by measuring the cyclic voltammogram of the electrolyte at the thin layer cells at a scan rate of 5 mV/s, so that steady-state conditions were achieved.

The triiodide diffusion coefficient $D_{I_3^-}$ is proportional to the diffusion-limited current density j_{lim} and was calculated via [16]:

$$D_{I_3^-} = \frac{j_{lim} l}{2nFc_{I_3^-}} \qquad (1)$$

where F is Faraday's constant, l the electrode distance reported above, and $c_{I_3^-}$ is the molar concentration of triiodide ions.
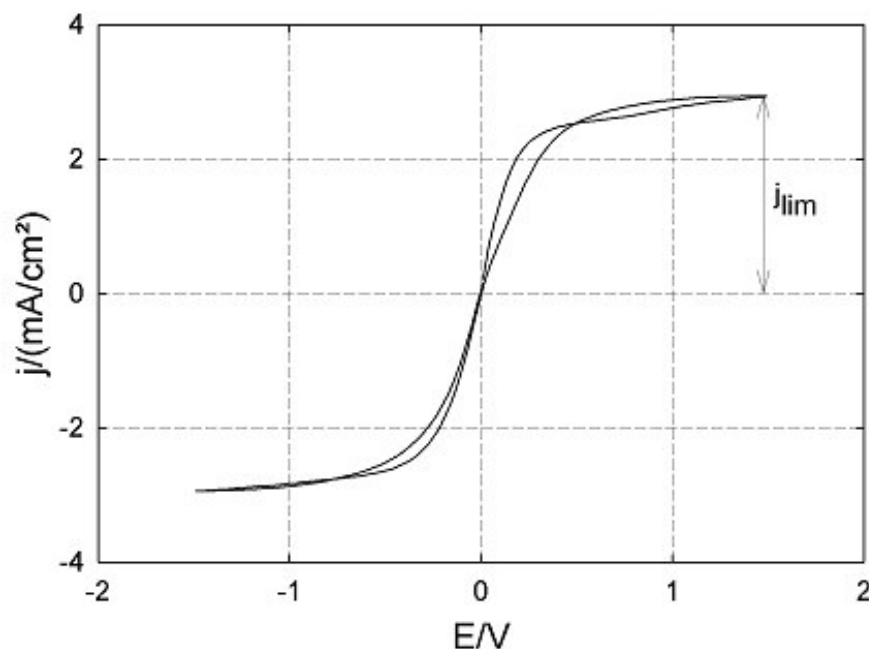

Figure 1. Polarization measurement of electrolyte B within a thin layer cell with $l = 31$ µm.

For a measured diffusion-limited current density of j_{lim} = 2.93 mA/cm² and a separately determined electrode distance of l = 31 µm a diffusion coefficient of $D_{I_3^-} = (4.7 \pm 0.6) \cdot 10^{-7}$ cm²/s

results. The given error was calculated by the error propagation law. The observed standard deviation from three measurements was $4.1 \cdot 10^{-9}$ cm²/s, showing an excellent reproducibility of this method.

Figure 2 shows a typical impedance spectrum of electrolyte B at a thin layer cell. The first part of the impedance spectrum is attributed to the kinetics at the platinum electrode [17], the second to diffusion processes. For the analysis of the impedance spectrum the equivalent circuit shown in Figure 3 was used. It consists of the following elements: the serial resistance R_S, including the resistances of the electrolyte, the TCO-coated glass and the cables, the charge transfer resistance R_{CT} of the two electrodes, the constant phase element CPE, which is employed instead of the usual double layer capacitance of the two electrodes, due to the roughness of their surface, and the Warburg impedance W_S, which is attributed to diffusion processes in the electrolyte.
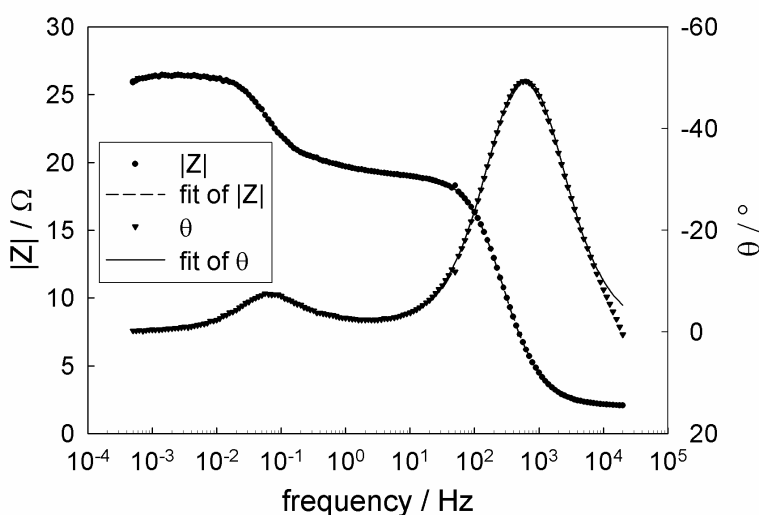

Figure 2. Impedance spectrum at a thin layer cell, electrode distance $l = 34$ µm, for details see text.

Figure 3. Equivalent circuit used for the analysis of the impedance spectrum including serial resistance R_S, charge transfer resistance R_{CT}, constant phase element CPE, and Warburg impedance W_S.

The impedance of the constant phase element is given by [18]:

$$Z_{CPE} = \frac{1}{B(i\omega)^{\beta}} \qquad 0 \le \beta \le 1 \qquad (2)$$

where ω is the angular frequency, B is the CPE parameter and β is the CPE exponent.

The finite Warburg impedance does only include the diffusion of the I_3^--ion, because the I^--ion is like a supporting electrolyte in a large excess and the diffusion coefficient of both species are in nearly the same order of magnitude. The impedance of W_S is given by [13,19]:

$$Z(\omega) = R_D \frac{\tanh\left(\sqrt{i\omega\tau_D}\right)}{\sqrt{i\omega\tau_D}} \tag{3}$$

where R_D has the dimension Ω, the parameter τ_D is associated to the diffusion coefficient and the Nernst-distance of δ to the electrode, where the concentration of the diffusion-limiting species is constant. For thin layer cells this constraint is fulfilled for a distance of $\delta = l/2$ and for τ_D follows:

$$\tau_D = \frac{\delta^2}{D_{I_3^-}} = \frac{(l/2)^2}{D_{I_3^-}} \qquad c_{I_3^-}(x = \delta, t) = const. \tag{4}$$

yielding the diffusion coefficient of the triiodide ion.

The fitting results are in a good agreement with measured impedance values. The values of the fitting parameter are listed in Table 1.

Table 1. Fitting parameter of the impedance spectrum.

R_S / Ω	R_{CT} / Ω	$B / Fs^{\beta-1}$	β	R_D / Ω	τ_D / s
2.134	16.73	$6.7051 \cdot 10^{-5}$	0.95526	7.455	6.897

For a distance between the electrodes of $l = 34\ \mu m$ and a value of $\tau_D = 6.897\ s$ a triiodide diffusion coefficient of: $D_{I_3^-} = (4.2 \pm 1.0) \cdot 10^{-7}\ cm^2/s$ results.

The diffusion coefficients obtained from both measuring methods are in a good agreement to each other.

A triiodide diffusion coefficient was already determined for an electrolyte mixture containing MPII and EMISCN [1] ($D_{I_3^-} = 2.95 \cdot 10^{-7}\ cm^2/s$). At this electrolyte composition the concentration of the low viscous EMISCN is smaller, entailing a lower diffusion coefficient, in accordance with expectation.

3.2. Electrochemical stability of the electrolyte components

Because of the observed instability of the electrolyte mixtures containing MPII and EMISCN, the electrochemical stability of MPII and EMISCN were studied. The stability windows were determined by cyclic voltammetry of a solution of MPII or EMISCN in AN with TEABF$_4$ as a supporting electrolyte. The cyclic voltammograms (CVs) of a solution of 0.1 mol/L MPII, 0.8 mol/L TEABF$_4$ in AN and of a solution of 0.1 mol/L EMISCN, 1.0 mol/L TEABF$_4$ in AN are shown in Figure 4. The CVs were measured at a scan rate of 10 mV/s and started in anodic direction.
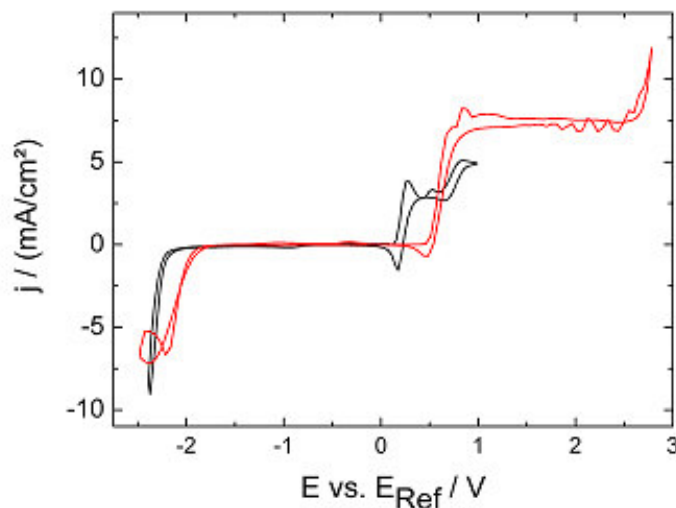
Figure 4. Cyclic voltammograms: (——): 0.1 mol/L MPII, 0.8 mol/L TEABF$_4$ in AN; (——): 0.1 mol/L EMISCN, 1.0 mol/L TEABF$_4$ in AN.

MPII is stable from about -2.0 V to about 0 V vs. the Ag/Ag$^+$-Kryptofix reference electrode, described above. On the anodic side of the voltage window two reactions are taking place; the first in a voltage range at about 0 V to 0.5 V, the second at about 0.5 V to 1.0 V. The reactions can be attributed to the oxidation of iodide to triiodide and the oxidation of triiodide to iodine [20]:

$$3I^- \rightarrow I_3^- + 2e^- \tag{5}$$
$$2I_3^- \rightarrow 3I_2 + 2e^- \tag{6}$$
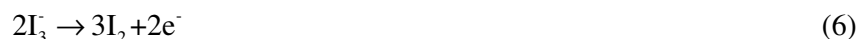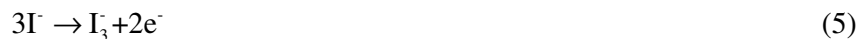
The EMISCN is electrochemical stable from about -1.8 V to 0.5 V. The anodic reaction is, as suggested by Pringle et al. [21], the oxidation of thiocyanate to the thiocyanogen:

$$2SCN^- \rightarrow (SCN)_2 + 2e^- \tag{7}$$

The thiocyanogen polymerizes to the red polythiocyanogen [22]:

$$\frac{x}{2}(SCN)_2 \rightarrow (SCN)_x \tag{8}$$

The occurrence of the polythiocyanogen was observed during the measurement as a red "dot" in the solution, which was increasing with time.

In Figure 4 it can be seen that the beginning of the oxidation of the thiocyanate is overlapping with the equilibrium of iodide/triiodide, which is the usually used redox-couple in DSCs. Therefore the application of EMISCN in dye-sensitized solar cells seems to be critical, especially when focusing on the long term stability of DSCs. While the DSC is working, thiocyanogen and afterwards

polythiocyanogen might be produced. Therefore for DSC electrolytes based on a binary mixture of ILs, the utilization of other ILs as a "solvent-IL" is recommended.

Table 2 shows voltage windows of other low viscous ILs (EMIDCA, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF$_4$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMINTf$_2$), and 1-ethyl-3-methylimidazolium trifluoromethan-sulfonate (EMIOTf)) recently measured in our lab that are more suited for application in DSCs.

Table 2. Electrochemical stability and viscosity of some ILs. Electrochemical stability was measured via cyclic voltammetry, WE: Pt, CE: Pt, RE: Ag/Ag$^+$-Kryptofix.

IL	cathodic limit	anodic limit	viscosity
EMIDCA	-2.0 V	1.5 V	21 mPa s [23]
EMIBF$_4$	-2.0 V	3.0 V	37 mPa s [24]
EMINTf$_2$	-2.0 V	2.5 V	28 mPa s [25]
EMIOTf [26]	-2.0 V	1.9 V	42.7 mPa s [27]

These ILs show an excellent electrochemical stability, thus no instabilities should be observed by the use of these ILs in DSC-electrolytes based on blends with MPII.

Among these ILs**,** EMIDCA has the lowest viscosity and also for electrolyte blends based on EMIDCA/MPII an improvement of the triiodide diffusion coefficient is obtained. [28]

4. CONCLUSIONS

The diffusion coefficient of I$_3^-$ in a binary IL mixture (EMISCN/MPII) was determined by two different methods (polarization measurements and impedance spectroscopy at thin layer cells) yielding two values for the diffusion coefficient, which are in a good accordance. At 25 °C a diffusion coefficient of $D_{I_3^-} = (4.7 \pm 0.6) \cdot 10^{-7}$ cm²/s was obtained by polarization measurements and $D_{I_3^-} = (4.2 \pm 1.0) \cdot 10^{-7}$ cm²/s by impedance spectroscopy for an electrolyte composition of 0.050 mol/L I$_2$ in a mixture of MPII and EMISCN (weight ratio 1:1). Thus with regard to charge transport in the DSC a binary electrolyte blend based on EMISCN seems to be promising, but problems in the application of EMISCN in a DSC arise from of electrochemical stability of EMISCN.

Voltage windows of MPII and EMISCN were determined by CV measurements. MPII is electrochemically stable in the voltage range -2.0 V to about 0 V vs. a non-aqueous Ag/Ag$^+$-Kryptofix reference electrode. In the voltage range of 0 V to 0.5 V and 0.5 V to 1.0 V two reactions were observed assigned to the formation of triiodide and iodine, respectively.

EMISCN is electrochemically stable from about -1.8 V to 0.5 V vs. an Ag/Ag$^+$-Kryptofix reference electrode. The anodic reaction is attributed to the oxidation of thiocyanate to thiocyanogen. CV-measurements show that EMISCN might not be used in DSCs when the redox-couple (I$^-$/I$_3^-$) is present, due to the formation of thiocyanogen and polythiocyanogen.

Therefore the substitution of EMISCN by other ILs with a sufficient electrochemical stability, e. g. EMIDCA, EMIBF$_4$, EMINTf$_2$, and EMIOTf, is recommended.

References

1. P. Wang, Shaik M. Zakeeruddin, R. Humphry-Baker and M. Grätzel, *Chem. Mater.*, 16 (2004) 2694.
2. B. O'Regan and M. Grätzel, *Nature*, 353 (1991) 737.
3. M. Grätzel, *J. Photochem. Photobiol. A*, 164 (2004) 3.
4. N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Petterson, A. Azam and M. Grätzel, *J. Electrochem. Soc.,* 143 (1996) 3099.
5. A. Hinsch, J. M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer and J. Ferber, *Prog. Photovolt: Res. Appl.*, 9 (2001) 425.
6. R. Kawano, M. Watanabe, *Chem. Commun.,* (2005) 2107.
7. P. Wang, Shaik M. Zakeeruddin, P. Comte, I. Exnar and M. Grätzel, *J. Am. Chem. Soc.*, 125 (2003) 1166.
8. S. Mikoshiba, S. Murai, H. Sumino, T. Kado, D. Kosugi and S. Hayase, *Curr. Appl. Phys.*, 5 (2005) 152.
9. P. Wang, Shaik M. Zekeeruddin, J.-E. Moser and M. Grätzel, *J. Phys. Chem. B,* 107 (2003) 13280.
10. K. Fredin, M. Gorlov, H. Pettersson, A. Hagfeldt, L. Kloo and G. Boschloo, *J. Phys. Chem. C*, 111 (2007) 13261.
11. A. Hauch and A. Georg, *Electrochim. Acta,* 46 (2001) 3457.
12. J. E. Baur and R. M. Wightman, *J. Electroanal. Chem.*, 305 (1991) 73.
13. K. Izutsu, *Electrochemistry in Nonaqueous Solutions*, Wiley-VCH, Weinheim (2002).
14. M. Zistler, P. Wachter, P. Wasserscheid, D. Gerhard , A. Hinsch, R. Sastrawan and H. J. Gores, *Electrochim. Acta*, 52 (2006) 161.
15. P. Wachter, C. Schreiner, M. Zistler, D. Gerhard, P. Wasserscheid and H. J. Gores, *Microchim. Acta*, in press, DOI 10.1007/s00604-007-0803-2.
16. A. T. Hubbard and F.C. Anson, in *Electroanal. Chem.,* Vol. 4, A. Bard, Editor, pp. 151-159, Marcel Dekker, Inc., New York (1970).
17. M. Zistler, P. Wachter, C. Schreiner, M. Fleischmann, D. Gerhard, P. Wasserscheid, A. Hinsch, and H. J. Gores, *J. Electrochem. Soc.*, 154 (2007) B925.
18. J. R. Macdonald, *Impedance Spectroscopy*, John Wiley & Sons, New York (1987).
19. J. R. Macdonald and D. R. Franceschetti, *J. Electroanal. Chem.*, 307 (1991) 1.
20. K. J. Hanson and C. W. Tobias, *J. Electrochem. Soc.*, 134 (1987) 2204.
21. J. M. Pringle, J. Golding, C. M. Forsyth. G. B. Deacon, M. Forsyth and D. R. MacFarlane, *J. Mater. Chem.*, 12 (2002) 3475.
22. A. F. Holleman and E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin (1995).
23. D. R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth and G. B. Deacon, *Chem. Commun.*, (2001) 1430.
24. T. Nishida, Y. Tashiro and M. Yamamoto, *J. Fluorine Chem.*, 120 (2003) 135.
25. A. B. McEwen, E. L. Ngo, K. LeCompte and J. L. Goldman, *J. Electrochem. Soc.*, 146 (1999) 1687.
26. J. Lodermeyer, PhD thesis, Regensburg (2006).
27. S. Zhang, N. Sun, X. He, X. Lu and Xiangping Zhang, *J. Phys. Chem. Ref. Data*, 35, (2006) 1475.

28. P. Wachter, M. Zistler, C. Schreiner, M. Berginc, U. Opara Krašovec, D. Gerhard, P. Wasserscheid, A. Hinsch and H. J. Gores, J., "Characterisation of DSSC-electrolytes based on 1-ethyl-3-methylimidazolium dicyanamide: Measurement of triiodide diffusion coefficient, viscosity, and photovoltaic performance", *J. Photochem. Photobiol. A,* in press, available online: doi:10.1016/j.jphotochem.2007.12.001