Impact of organic solvents in combination with redox-couples on magnitude of seebeck coefficient, and electrical current in thermoelectric generators

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In previous work it was shown that Ionic Liquids as active substances in thermoelectric generators have the potential to reduce the thermal conductivity as compared to Solid State materials used in conventional TEGs. Furthermore, it was observed that the Seebeck coefficient could be significantly increased. After a large variety of experiments, it appears that the remaining bottleneck coming to high performance TEGs is, first finding ILs with increased negative Seebeck coefficient, and, second sufficient current extraction. Looking at the current it appears, that higher extractions for a given redox-couple concentration are favoured at reduced viscosity. On the way to explore the effect of viscosity-induced current limitation, in a first step, the Ionic liquids are substituted by a low-viscosity organic solvent such as propylene carbonate (PC). The results showed that, indeed, the thermo-current increases significantly. It was further found that the Seebeck coefficient (SE) using PC exhibited values as high as 1.7 mV/K. Such high values were in previous work rather attributed to the use of ionic liquids. Surprisingly, by adding up to 10% of water to PC, the increased current allowed doubling the power, compared to pure PC. The paper studies the effect of combinations of solvent and redox-couples and tries to correlate the effect of water in PC looking at physical properties such as viscosity, but also the effects of charged carrier-attachment at the electrodes.
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1. Introduction

Ionic liquids (ILs) were chosen as active substances in thermoelectric generators (TEGs) because of their chemical and thermophysical properties like high thermal stability, low vapor pressure, low thermal conductivity, and, the potential of reducing harmful substances to the biosphere at recycling and failure-based breakage [1]. Redox-couple with low redox-potential must be mixed in the ILs for carrier extraction. ILs are like molten salts with high molarity. Surprisingly high voltages (high SE-values) can be induced for a large number of ILs by a temperature gradient between the electrodes in a thermo-electrochemical cell. To achieve voltages that are sufficient for driving electronic devices, the thermo-voltage must be further improved and individual thermocells must be connected serially. Therefore, the cells must be alternatively filled with such ILs which deliver positive and negative SEs. Using single test-cells, several series of ILs were screened

in order to identify the factors that influence the polarity, the magnitude of SE, and the power output of the test-cells.

Normally, output voltage of thermal asymmetric TEG-electrodes with redox-couple as charger carriers, is expressed by the entropy change of the redox reaction. It was found that for ILs, additionally to the choice of redox-couples and their concentrations, SE depends on multiple properties such as cations, functional groups of anions of the IL and the choice of electrode material [2–4]. In particular, Sosnowska et al. [5] found that the structural features of particular ions of the IL could describe the value of SE. Such features include the size, symmetry, and branching of the cation. Relatively symmetric cations, along with high electron-binding energy anions can also influence SE.

We therefore assume that all present molecules (Ions of IL and redox-couple) can participate to create the first electrical layers at the electrode-fluid interface, where electrical charge transfer occurs. The resulting double layer can be considered as dependent

on temperature and on the material-properties of electrodes and fluid [6,7]. Thus, the concentration of ions at the surface in a finite volume is entirely different from the bulk-fluid, where molecules uniformly distributed. Moreover, C. Rodenbücher et al. [8] indicated that the formation of a layered structure at the interface is beyond the classical double layer of Gouy-Chapman-Stern theory. It was found that the formation significantly depends on the specific ionic liquid and additives in use. It was considered that a dense short-range nanostructure, followed by a long-range double layer exists simultaneously. However, due to the temperature gradient between the electrodes, the specific and/or electrostatic adsorption processes at the electrode lead to asymmetric characteristics of the double layer. Also, we might consider the electrical current transfers from one electrode to the other a movement initiated by diffusion, migration and convection, depending on the position of the charge carriers relative to the electrode.

Simply said, we can assume that close to the interface a dense finite layer is formed, followed by a more distant double layer where the electrical potential decreases with respect to the distance. Further away, the molecules are considered as uniformly distributed in the bulk liquid. Because of the thermal asymmetry between the electrodes, a thermal gradient takes place and have reasonable grounds to force a strong convection movement in the liquid.

In consequence, charge carriers must pass through the diffusion- and double layer to carry the charge into the electrode. Therefore, temperature and viscosity can be seen as main parameters for the diffusion flux. Investigation of Cabral et al. [9] in electrochemical cells without thermal gradient between the electrodes, revealed that the diffusion coefficients of $Co^{2+/3+}$-redox-couple are clearly related to the viscosity of the solvent, being higher in solvents with lower viscosities. Strong convection

can significantly change the double layer thickness, with the effect that conditions for diffusion and thus the current density change significantly. Another recent study showed that the mass transfer resistance is the most dominant type of resistance for all the tested conditions and the charge transfer kinetics is found to be controlled by the electrolyte viscosity [10]. The correlation of the viscosity and the current allows to conclude how the mobility of charge carriers depends on viscosity of IL.

2. Experimental

The use of organic solvents added to the IL is considered as a strategy for reducing the viscosity of the fluid. To investigate this dilution effect, two ILs with different viscosities (see Table 1) were mixed with PC with an emphasis on increasing the ions mobility. To allow current extraction out of the test-cell, 0.01 mol/L of redox couple $Co^{2+/3+}(bpy)_3(TFSI_2)_{2/3}$, later abbreviated by $Co^{2+/3+}$, was added for all measurements. Note, for such systems the carrier transport is 1:1 linked to material transport. For better comparison, the redox-couple concentration (0.01 mol/L $Co^{2+/3+}$) was kept constant in all studied fluids systems, namely ILs, ILs-PC (1:1) mixture and PC solvent only. The current–voltage-power characteristics were performed in a test-cell described in previous publication [12]. IL is poured in a silicone ring that is squeezed between two Rhodium coated sapphire electrodes (with an electrode-surface of 1.77 cm^2) and clamped by two aluminum blocs. The aluminum parts are connected to a cooling circuit, respectively a heating system. On both sides the temperature can be monitored and controlled. The system allows to measure the difference of potential under load and open circuit conditions.

The Ionic liquids were delivered from Solvonic (France), PC was purchased by Merck (Germany) and redox-couple $Co^{2+/3}$ by Lumtec (Taiwan).

3. Results and discussion

SE-coefficients were determined for a series of ILs and values were correlated to viscosity to get an insight into how viscosity participates to voltage generation. The measurements revealed no correlation of SE- and viscosity values (see Fig. 1a).
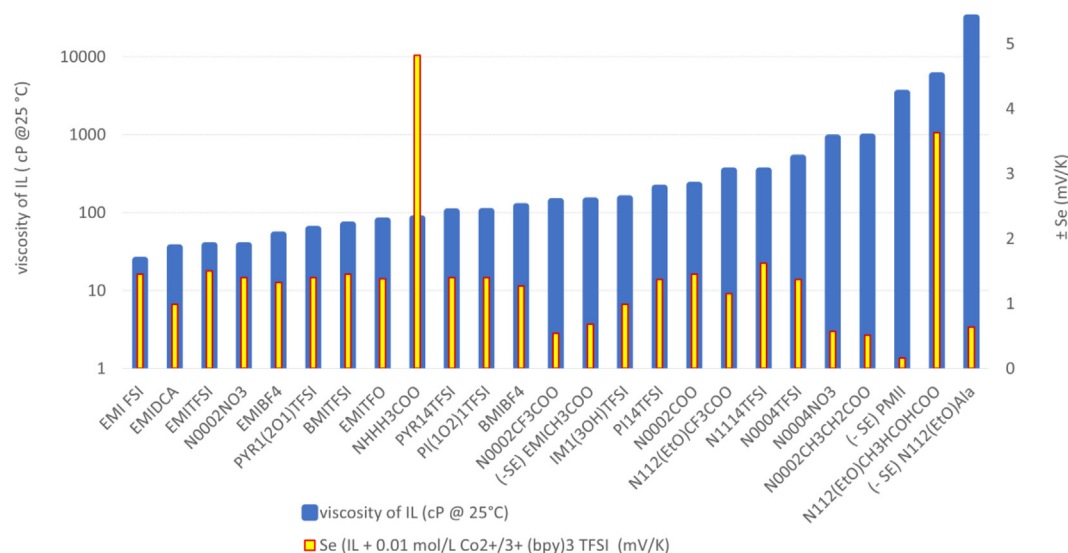
Table 1
Properties of PC and used ILs.

Abbreviation	Fluid	Viscosity (mPa.s at 25 °C)
P66614 TFSI	Trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl)imide	318
EMI TFSI	1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl)imide	35.6
PC	Propylene carbonate	2.5

Fig. 1a. Overview over viscosity and [±] SE-values for ILs containing 0.01 mol/L $Co^{2+/3+}$ redox-couple: no significant correlation can be observed. ILs with negative SE-values are labeled with (-SE).

To determine whether viscosity correlates with current densities, the current flow of a series of IL (with FSI/TFSI as anion) were measured at $\Delta T = 90$–108 K between the electrodes with $T_{cold} = 22$–25 °C (Fig. 1b).

If we take into consideration that current exchange depends on the slowest part of the overall reaction, the reaction on the cold electrode would be rate-limiting and the impact of viscosity at the cold electrode would be significant.

Consequently, it can be concluded that the current decreases significantly at viscosities of ILs between 24.5 and 61 mPa.s (measured at 25 °C).

Subsequently, two ILs with different viscosities were chosen and diluted with PC. SE and power output were measured at two temperature ranges. The experiments were conducted at two different temperatures for the hot electrode (T_{hot}), first at 50–55 °C and second at 92–95 °C (except for EMI TFSI diluted in PC, for which the T_{hot} only reached 72 °C) whereby the temperature of the cold electrode (T_{cold}) is kept constant at 20–23 °C. The obtained data for the SE-values and power outputs are summarized in Table 2. Note, the power values in Table 2 were taken at the maximum power point (MPP). Both ILs show a positive SE. As expected, the value of SE is not changing with increasing temperature of the hot electrode. Compared to the SE values of undiluted ILs, an increase of about 100 μV/K is obtained for both ILs diluted (1:1) (v/v) in PC. Surprisingly, the SE value of PC is as high as the SE measured for the undiluted IL. A strong increase of power output at MPP was measured for both ILs in PC. It has been shown that solvent PC pure (with 0.01 mol/L $Co^{2+/3+}$) shows the highest power output of 52 mW/m² (at 70 K).

In a further step, the impact of low viscous solvent (PC) on the transport of electrical current in ILs was studied at different temperature regimes. For this, the current of EMI TFSI and EMI TFSI + PC (1:1; v/v) was measured at different temperatures by increasing the temperature of the hot electrode (see Fig. 2). As expected, the current increases by increasing temperature but not with the same rate. The current measured for diluted EMI TFSI increases about 4 times compared to undiluted EMI TFSI. The dilution with PC will decrease the viscosity of the mixture, hence increasing the rate of the current increase. All tests were run with 0.01 mol/L $Co^{2+/3+}$.

The same experiments were made with PC diluted with water in different concentrations (1%, 10% and 50% H_2O in PC (v/v)). It was found that the current increases by increasing temperature, but also by increasing the content of water. The increase in current saturated for concentrations higher than 10% H_2O in PC. Hence, there is an optimum ratio between highest current and lowest water concentration observed for 10% H_2O in PC. At his dilution, values of about 140 mA/m², respectively 70 mW/m² were measured at a difference of 64 K between the two electrodes.

However, a closer consideration of the power output at MPP (see Fig. 3) of the series of PC and PC with different water content revealed an increase of power of more than 3 times for test with H_2O at 33 K temperature difference between hot and cold electrodes (22 °C for T_{cold} and 55 °C for T_{hot}).

Adding 1% of water to PC can double the power output. Highest power at MPP was measured for 10% of water in PC. Adding 30% or 50%, increases the power similarly, but not in the same strength.

Power output at MPP was calculated as a function of voltage for PC, PC + 1% H_2O, PC + 10% H_2O, PC + 30% H_2O and PC + 50% H_2O. Power increases for fluid with 10% of H_2O in PC (v/v) more than 3 times compared to pure PC. Adding 1% of water to PC can double the power output. We have to consider that the solubility of water in PC is only 240 g l^{-1} (at 20 °C) and $Co^{2+/3+}$ - redox-couple is considered as insoluble in water.

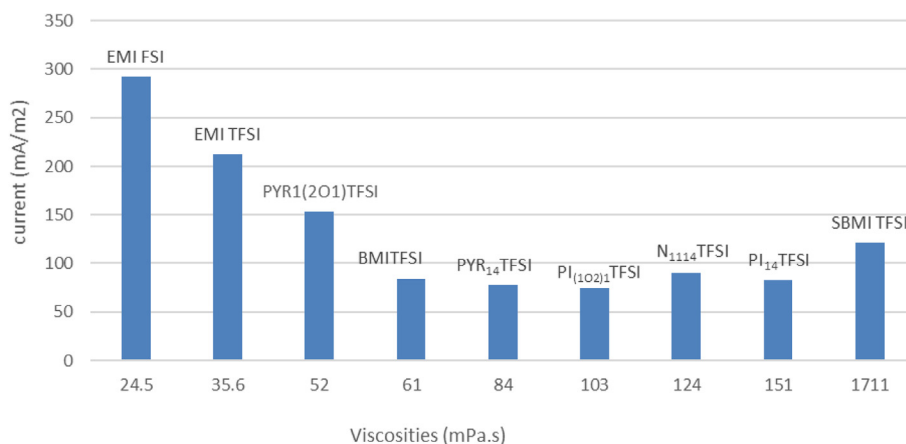**Fig. 1b.** Current (mA/m²) of 0.01 mol/L $Co^{2+/3+}$ in ILs with TFSI/FSI anion and different cations at a difference of 90–108 K between both electrodes at T cold = 20–25 °C.

Table 2
SE-coefficients and Power at MPP of two ILs: P66614 TFSI and EMI TFSI, the PC-diluted ILs (1:1; v/v), and PC pure at two different temperatures regimes.

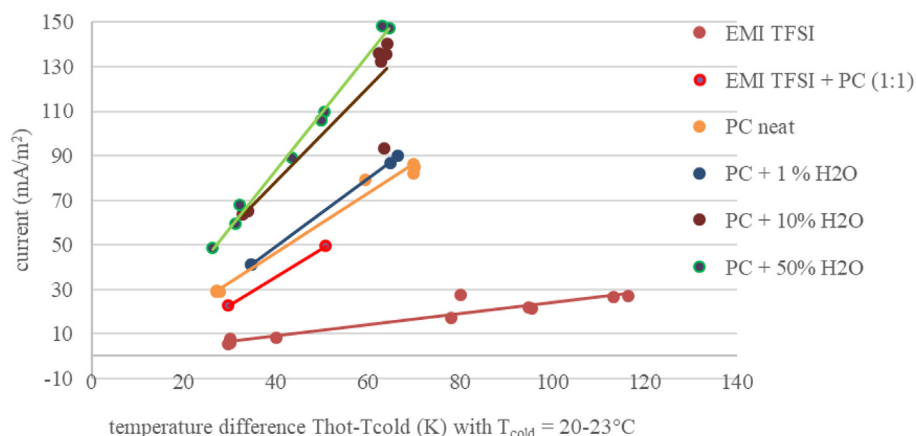| Fluid	SE (μV/K) T cold 20–23 °C T hot 50–55 °C	SE (μV/K) T cold 20–23 °C T hot 92–95 °C	Power at MPP (mW/m²) T cold 20–23 °C T hot 50–55 °C	Power at MPP (mW/m²) T cold 20–23 °C T hot 92–95 °C
P66614 TFSI	n.m.	1760	n. m.	0.68
P66614 TFSI + PC (1:1) (v/v)	1863	1867	5.60	36.64
EMI TFSI	1526	1518	1.81	13.30
EMI TFSI + PC (1:1) (v/v)	1641	1633*	3.55	17.14
PC	1756	1747	6.19	52.63

* T_{hot} = 72 °C; n. m. = not measured.

Fig. 2. Current as a function of temperature for EMI TFSI, EMI TFSI + PC (1:1; v/v), P66614 TFSI, P66614 TFSI + PC (1:1; v/v) and PC mixed with water in different concentrations (1%, 10% and 50% H2O (v/v)) . All tests run with 0.01 mol/L Co2+/3 + with T_{cold} = 20–23 °C.
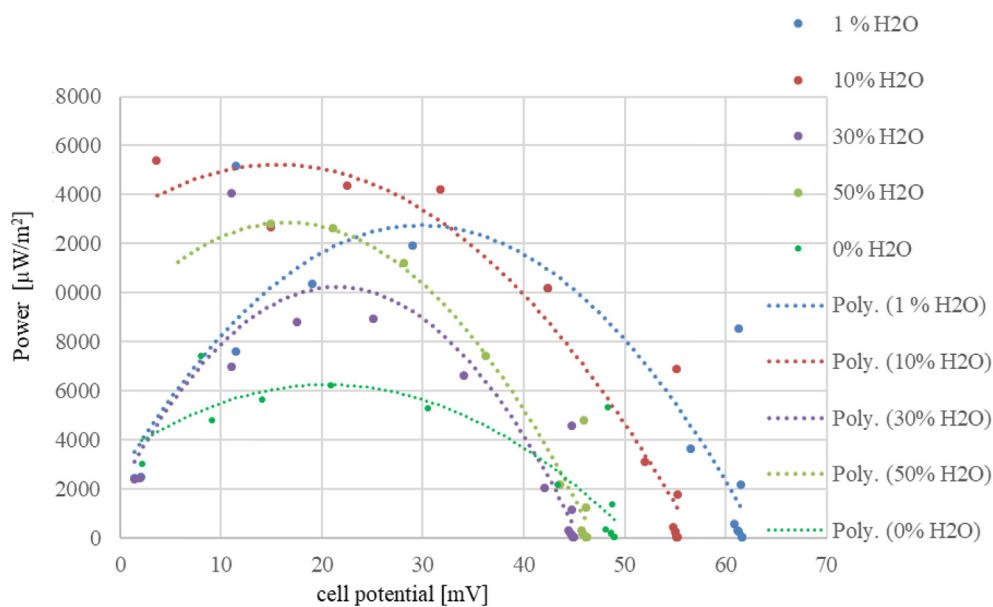

Fig. 3. Measurement of power output at MPP as a function of voltage for PC, PC + 1% H_2O, PC + 10% H_2O, PC + 30% H_2O and PC + 50% H_2O within the temperatures of 22 °C for T_{cold} and 55 °C for T_{hot}. Power increases for fluid with 10% of H_2O in PC (v/v) more than 3 times compared to PC pure. Adding 1% of water to PC can double the power output. Increasing water-concentration to 30% and 50% the power output decrease, despite of decreasing of viscosities.

4. Conclusion

It was shown that for different kinds of ILs the SE-coefficients could not be correlated with viscosity. However, regarding ILs with different sorts of cation but the same anion (TFSI) a correlation could be measured, and a significant current decrease was observed for viscosities higher than 52 mPas.s.

In addition, we could show that the SE values increases when ILs are diluted with a low viscous solvent (PC). Furthermore, PC shows higher SE value and current than undiluted ILs.

Additionally, we studied the effect of the dilution of PC with water on the transport of electrical current. We measured an increase of the current with both increasing temperature and water dilution. Thus, adding 1% of water to PC can double the power output compared to measurements of non-diluted PC. Adding 10% water to PC will lead to the highest rise of electrical current of about 140 mA/m², respectively 70 mW/m² for a difference of temperature of 64 K.

CRediT authorship contribution statement

Edith Laux: Conceptualization, Methodology, Data curation, Writing - original draft, Writing - review & editing. **Laure Jeandupeux:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing. **Alexandra Homsy:** Conceptualization, Methodology, Data curation. **Martin Hofmann:** Conceptualization, Methodology, Data curation. **Philippe Potty:** Writing - original draft, Writing - review & editing. **Herbert Keppner:** Conceptualization, Methodology, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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