New generation of thermogalvanic cells: design, development and performance

"NOCTURNE"

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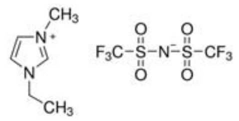
The thermogalvanic cells are promising devices for the conversion of low grade heat into electricity. Their functioning is based on the generation of a potential difference between two identical electrodes, when there is a temperature gradient in a solution. One of the critical points to achieve a high thermoelectric effect is a choice of convenient redox couples and electrolytes. Among all solvents, ionic liquids attract a lot of attention because of their interesting physicochemical properties. Moreover, it is expected that ionic liquids, being highly structured environments, will increase Seebeck coefficients via solvation and reorganization phenomena. The main objective of this project was therefore the search for a suitable system (redox couple - ionic liquid) to develop new performant thermogalvanic devices.

Ionic liquid: EMIMTFSI

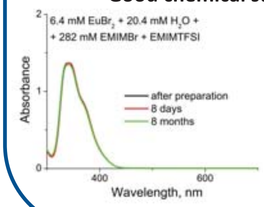
- Ionic liquid with a melting point at -16 °C and a boiling point at 455 °C
- Ionic conductivity of 10 $mS.cm^{-1}$
- Thermal conductivity of 0.12 $W.m^{-1}.K^{-1}$, 1/6th of water
- Dynamic viscosity of 33 cP
- 5.4 V electrochemical window

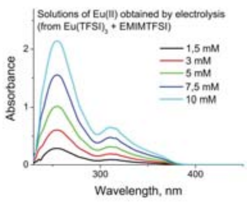


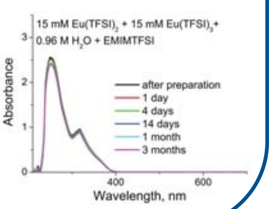
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
EMIMTFSI

Redox couple: europium(III)/europium(II)

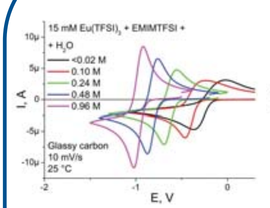
Good chemical stability in the presence of water in EMIMTFSI

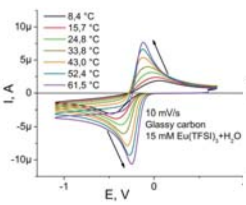


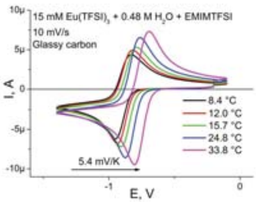


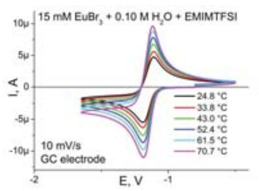


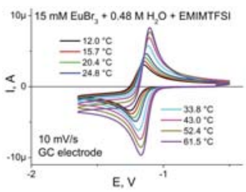
Electrochemical properties of $Eu(TFSI)_3$ and $EuBr_3$











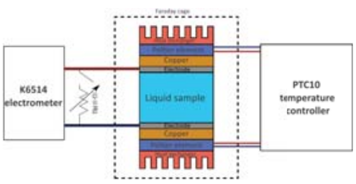
Reference electrode: Ag^+/Ag

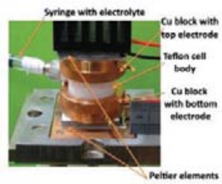
Redox couples:

- $[Eu(TFSI)_x]^{3-x/2-x}$
- $[Eu(H_2O)_{9/8}]^{3+/2+}$
- $[Eu(Br)_y]^{3-y/2-y}$
- $[Eu(TFSI)_x(H2O)_n(Br)_y]^{3-x-y/2-x-y}$

Quasi-reversible diffusion-controlled electrode process: Eu^{III}/Eu^{II}

Seebeck coefficient (S_e) and power measurements





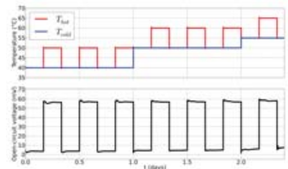
Home-made thermoelectric cell with Glassy carbon electrodes

- V = 170 µl
- $d_{electrodes}$ = 6 mm

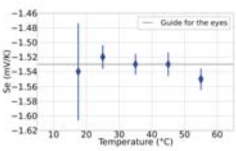
Seebeck coefficient: $S_e = \frac{\Delta E}{\Delta T} = \frac{\Delta S}{nF}$

Figure of merit: $ZT = S_e^2 \cdot \frac{\sigma}{\kappa} \cdot T$

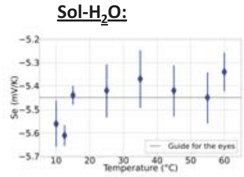
σ: electrical conductivity
κ: thermal conductivity
F: Faraday constant
n: number of the exchanged electrons
ΔS: entropy of the redox reaction

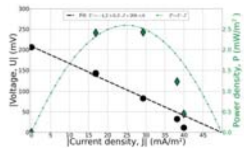


Sol-anhydrous:



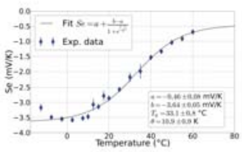
Sol-H_2O:

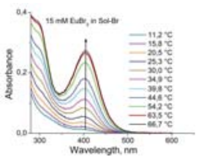


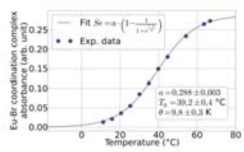


Huge Seebeck coefficient measured with Sol-H_2O

Sol-Br:







Temperature increase : |Se| decreases from 3.5 mV/K to 0.5 mV/K

Solutions	Configuration	T_{mean}, °C	ΔT, K	R_i, kΩ	P_{max}, $mW.m^{-2}$	η_r, %
Sol-H_2O	Hot/Cold	40	40	800	0,63	$7 \cdot 10^{-4}$
		37,5	55	2120	0,37	$2 \cdot 10^{-4}$
	Cold/Hot	40	40	150	2,55	$9 \cdot 10^{-4}$
Sol-Br:	Hot/Cold	40	40	140	0,38	$4 \cdot 10^{-4}$
		35	60	270	0,59	$3 \cdot 10^{-4}$
	Cold/Hot	40	40	64	0,68	$2 \cdot 10^{-4}$
		15	40	1040	0,12	$4 \cdot 10^{-5}$

Solutions

15 mM $Eu(TFSI)_2$ + 15 mM $Eu(TFSI)_3$ or 15 mM $EuBr_2$ + 15 mM $EuBr_3$ in

- **Sol-anhydrous**: pure EMIMTFSI with $[H_2O]$<200 ppm
- **Sol-H_2O:** EMIMTFSI with 0.48 M H_2O
- **Sol-Br:** EMIMTFSI with 0.48 M H_2O and 1.37 M Br^-

Conclusions

Seebeck coefficient in EMIMTFSI with Eu^{3+} / Eu^{2+} redox couple was investigated for the first time: *world record values were obtained*.
Importance of complexation was highlighted: the nature of ligands and their concentration have a strong influence on the measured S_e.

Next steps

Increase power with higher concentrations of redox species and temperature difference.
Exploit ligand effects in other IL-redox combination systems.

AKNOWLEGEMENTS

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