Master 2 Internship

Thermoelectric energy conversion in ionic liquids: a study of new redox systems

Thermoelectricity, a materials' capability to convert heat in to electric energy has been known to exist in liquids for many decades. Unlike in solids, this conversion process in liquids take several forms including the redox reactions, the thermodiffusion of charged species and the temperature dependent formation of electrical double layer at the electrodes. The observed values of Seebeck coefficient (Se = - ΔV/ΔT, the ratio between the induced voltage (ΔV) and the applied temperature difference (ΔT)) are generally above 1 mV/K, an order of magnitude higher than those found in the solid counterpart. The first working example of a liquid-based thermo-electrochemical (TEC) generator was reported in 1986 using $Fe(CN)_6^{3-/4-}$ redox couple in water. However, due to the low ionic conductivity of liquids, its conversion efficiency was very low, preventing their use in low-temperature waste-heat recovery applications. The outlook of liquid TEC generators brightened in the last decade with the development of ionic liquids (ILs). ILs are molten salts that are liquid below 100 °C. Compared to classical liquids, they exhibit many favorable features such as high boiling points, low vapour pressure, high ionic conductivity and low thermal conductivity accompanied by higher Se values. More recently, an experimental study by IJCLab and SPEC (CEA-Saclay) revealed that the complexation of transition metal redox couples in ionic liquids leads to enhancing their Se coefficient by more than a three-fold from -1.6 to -5.7 mV/K, one of the highest values reported in IL-based TEC cells. A clear understanding and the precise control of the speciation of metal ions therefore is a gateway to the rational design of future TEC liquids. Based on these recent findings, we propose an experimental study on the chemistry of transition metal redox ions in ILs and mixtures. A long-term goal associated to the present project is to demonstrate the application potential of liquid TEC cells based on affordable, abundant and safe materials for thermal energy harvesting as an energy efficiency tool.

To tackle the aforementioned challenges (both fundamental and technological), we propose a parametric study on the chemical and redox behavior of metal species (Fe, Cu and Ce) in ILs as a function of temperature and solution composition (ligands, different types of ILs and their mixtures). A speciation study on the interactions of metal ions with simple inorganic and organic ligands in ILs will be carried out by ***various electrochemical and spectrophotometric methods***. These IL/redox mixtures will undergo a systematic ***thermogalvanic characterization (open-circuit Se-coefficient and the power-output measurements)***. The combined results will be a dataset revealing the relationship between the physico-chemical descriptors (redox potential and stability constants of metal complexes) of the IL/redox combinations and their thermoelectric properties, which will be compared to the numerical simulation (not of the intern project) studies by the IJCLab group. Together, we aim to decipher the underlying electrochemical mechanisms of thermoelectric energy conversion in ILs and simultaneously, to identify the most socio-economically viable materials for their future development.

The following internship program is established for a 5 months' period, but can be adjusted according to the requirements by the Master's program of the candidate. After a brief introduction to the theoretical background and the existing literature in related fields of

research, the student will first undertake the electrochemical tasks at IJCLab. These include, **Task 1) Speciation of metal ions** (Fe, Cu and/or Ce) in ILs as a function of temperature and ligand content (halide ions, dicyanamide and/or sulfobetaine); and **Task 2) Redox properties of transition metal complexes** as a function of temperature and solution composition. The compound 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM.TFSI) is first considered as the most stable IL that is known to possess high Se coefficient (with Co salts), however other ionic liquids will also be considered. Once the speciation step is achieved, the liquid samples will be tested for their **thermoelectric properties** at SPEC **(Task 3)**. These results will be compared to the electrochemical characterization (task 2) and the numerical simulations (not part of the internship) from IJCLab. Depending on the advancement of the program, additional characterizations (e.g., affinity capillary electrophoresis, IJCLab) may be envisaged.
The funding for a PhD thesis on this subject is available.

Candidate profile
The candidate must be enrolled in Masters' program in Chemistry (Physical, Analytical or Inorganic) or in Physics (specialization in Thermodynamics or Energy sciences). Double majoring in Chemistry/Physics will be highly appreciated. The position requires a solid knowledge in solution chemistry, physicochemical characterization methods, thermodynamics and/or renewable energies. Good oral and written communication skills as well as data analysis skills are also required. We seek candidates with a strong motivation and curiosity in electrochemical and thermoelectric energy phenomena, autonomy and the capacity to work in a team in a highly interdisciplinary and collaborative project.

The application must include: detailed CV, 1-page cover letter, academic transcripts from L3, Masters' 1 and 2 or equivalent.

Application deadline: 01/12/2023

Contact information:

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