PhD thesis position

New redox systems for efficient thermogalvanic conversion of energy in ionic liquids

Workplace: IJCLab/Paris-Saclay University (50%) and CEA-Saclay (50%), France

Supervisors: Dr. Veronika ZINOVYEVA, Dr. Vladimir SLADKOV, Dr. Sawako NAKAMAE

Expected date of employment: 01/09/2023

Application: https://emploi.cnrs.fr/Offres/Doctorant/UMR9012-AMAMOL-005/Default.aspx

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Description of the thesis subject

This PhD study is part of an ongoing ANR project entitled "WH-RECOLTE," involving 3 laboratories (SPHYNX/SPEC/IRAMIS/CEA-CNRS, IJCLab/CNRS- Paris-Saclay University and PHENIX/CNRS-Sorbonne University). The project's goal is two-fold: to advance our current understanding of the thermal-to-electricity energy conversion mechanisms in complex liquids, and to demonstrate the true potential of liquid thermoelectric technology for waste heat recovery applications. More specifically, we aim to obtain robust liquid thermoelectric (TE) materials and devices based on ionic liquids and colloidal suspensions that are cost-effective, non-toxic and scalable, surpassing the current state-of-the-art TE-liquids. The main application will be the small scale (1~100 W) power generation from external heat flow (waste and ambient). The fundamental knowledge of WH-RECOLTE can also be extended to applications outside of renewable energy research, such as temperature and chemical pollutant sensors.

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 ($Se = - \Delta V/\Delta T$, 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. However, due to the low ionic conductivity of the liquids, their TE conversion efficiency remains very low, preventing the use of conventional thermogalvanic cells (based on water and organic solvents) in low-temperature waste heat recovery applications. The prospects for this technology have brightened in the last decade with the development of ionic liquids (ILs) [1-3]. ILs are molten salts with melting points below 100 °C. Compared to conventional liquids, they exhibit many favorable physicochemical properties such as high boiling point, low vapor pressure, high ionic conductivity and low thermal conductivity as well as their higher Se values. More recently, an experimental study conducted by IJCLab and SPEC revealed that record-high Se values can be achieved through competitive complexation phenomena of transition metals in ionic liquids. Understanding the chemical speciation in solution and the redox properties of the medium is therefore a very important step towards the rational design of thermogalvanic cells.

In this context, the proposed PhD project is built around a fundamental research on the chemical nature of the redox species (Fe, Cu, Ce…) in ionic liquids as a function of temperature and the surrounding solvent composition and its impact on the Se coefficient and the power output. The obtained results will reveal the intricate relationship between the physico-chemical parameters (e.g., redox potential, stability constants of the metallic complexes) and the thermogalvanic properties in ionic liquids, with a long-term objective of developing a new class of innovative device for the waste/ambient heat recovery.

Detailed presentation of the research project

The proposed PhD thesis is experimental, exploring first the fundamental properties (chemical, electrochemical, physico-chemical and thermogalvanic) of transition metal ions within the ionic liquid environment through several electrochemical and physico-chemical methods. These experiments are to be conducted in the framework of collaborative research between partner laboratories: the thermogalvanic measurements at SPHYNX/SPEC/CEA, metal complexation and spectral & electrochemical characterizations at IJCLab/ Paris-Saclay University; while interacting strongly with PHENIX/CNRS/Sorbonne University for the dispersion of colloidal particles in the presence of redox metal complexes [4].

The PhD research program thus contains several steps:

1) The speciation of metallic ions (initial focus on Ce, Fe and Cu) in ionic liquids and in IL/organic solvent mixtures, as a function of temperature and ligands by spectral methods at the IJCLab. Additionally, the interaction between the metallic ions and hydrophilic ligands will be studied by affinity capillary electrophoresis in aqueous solutions [5-6];
2) The redox properties of metal-complexes in ionic liquids via electrochemical methods (cyclic voltammetry, chronoamperometry, electrochemical impedance spectroscopy, and numerical simulations) and the electrolysis testing of solutions at the IJCLab;
3) The thermogalvanic measurements on selected systems (Se coefficient and power output) and the device optimization at SPHYNX;
4) The compatibility study of the bespoke redox couples with the colloidal dispersion (in collaboration with PHENIX). Numerous testing of such complex liquids for their chemical, electrochemical and thermal stability will be conducted.

The physico-chemical properties of the liquid media (viscosity, density, ionic conductivity, residual water content) will also be investigated.

Material and financial scientific conditions of the research project

The proposed PhD research work is financed entirely by the ANR WH-RECOLTE project. All equipment necessary for the realization of the project will be made available/accessible at the host laboratory or within the Paris-Saclay University's technology platforms.

Objective of promoting the research work of the PhD student

The PhD student is expected to present his/her thesis research work at various international and national conferences and workshops. The results will also be published in international scientific journals (peer-reviewed).

Bibliographical references

[1] V. Zinovyeva, S. Nakamae, M. Bonetti, M. Roger. Enhanced Thermoelectric Power in Ionic Liquids. ChemElectroChem, 1 (2014) 426-430.

[2] M. Bonetti, S. Nakamae, B.T. Huang, T. J. Salez, C. Wiertel-Gasquet, M. Roger. Thermoelectric energy recovery at ionic-liquid/electrode interface. J. Chem. Phys., 142 (2015) 244708.

[3] M.F. Dupont, D.R. MacFarlane, J.M. Pringle. Thermo-electrochemical cells for waste heat harvesting – progress and perspectives. Chem. Commun., 53 (2017) 6288-6302.

[4] K. Bhattacharya, M. Sarkar, T. J. Salez, S. Nakamae, G. Demouchy, F. Cousin, E. Dubois, L. Michot, R. Perzynski, and V. Peyre. Structural Thermodiffusive and Thermoelectric Properties of Maghemite Nanoparticles Dispersed in Ethylammonium Nitrate. ChemEngineering, 4 (2020) 5.

[5] Sladkov, V. Affinity capillary electrophoresis in studying the complex formation equilibria of radionuclides in aqueous solutions. ELECTROPHORESIS, 37 (2016) 2558–2566.

[6] Sladkov, V., Roques, J. & Meyer, M. Assignment of complex species by affinity capillary electrophoresis: The case of Th(IV)-desferrioxamine B. ELECTROPHORESIS, 41 (2020) 1870–1877.

Context of work

The PhD research work be conducted at two sites:

- IJCLab – UMR 9012 – CNRS/Université Paris-Saclay (Pôle Energie et Environnement, Pôle Physique Santé), under direction of Dr. Zinovyeva Veronika and Dr. Sladkov Vladimir;
- SPEC – UMR 3680 CEA/CNRS (laboratoire SPHYNX), under direction of Dr. Nakamae Sawako.

Le laboratoire de Physique des 2 Infinis Irène Joliot-Curie (https://www.ijclab.in2p3.fr/) belongs to the CNRS, the University of Paris-Saclay and the University of Paris, founded in 2020 merging of five UMRs located on the university campus of Orsay: the Center for Nuclear Sciences and Matter Sciences (CSNSM), the Laboratory of Imaging and Modeling in Neurobiology and Cancer (IMNC), the Institute of Nuclear Physics of Orsay (IPNO), the Linear Accelerator Laboratory (LAL), and the Theoretical Physics Laboratory (LPT). The IJCLab's research themes include nuclear physics, high-energy physics, astroparticles and cosmology, theoretical physics, particle accelerators and detectors, as well as the technology and application developments for energy, health and the environmental applications. Currently, the IJCLab counts about 280 engineers and technicians among its staff.

The SPHYNX lab of CEA-Saclay (https://iramis.cea.fr/spec/SPHYNX/) created in January 2012, consists of 18 permanent researchers, engineers and technicians from CEA and CNRS. Our active research efforts encompass a wealth of multidisciplinary characters; theoretical, numerical and experimental, to study physical systems that are far from equilibrium. Statistical physics of equilibrium systems provides today a well-established framework for classical thermodynamics. However, most 'real world' systems found in condensed matter, biology, natural or industrial macrocosms are out-of-equilibrium, either because of the presence of external forcing or because they cannot relax back to equilibrium. These systems are often non-linear, disordered and/or complex and present emerging properties of their own. The goal of SPHYNX is to gather researchers working on different objects but using common tools, those of the statistical physics to tackle the same challenge, that of complexity.

Constraints and risks

The PhD student must be able to undergo a medical visit to be able to handle chemical products.
The PhD student is expected to make frequent transfers between the two sites (IJCLab in Orsay and SPHYNX/SPEC in Gif-sur-Yvette).

Supplementary information/Candidate profile

The candidate must have a Masters' (M2 in France) in Physics (specialization in Thermodynamics or Energy sciences) or in Chemistry (Physical, Analytical or Inorganic). 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 (French and English required) and 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, two references (or more), 1-page cover letter; 1-page summary of the Masters' thesis, academic transcripts from Masters' 1 and 2 or equivalent.

NB. Due to the IJCLab's *RRA* (restricted area) classification, the recruitment is *conditional* upon HFSD approval. Consequently, the starting date is given as an indication and may be postponed.

Application deadline: 31/08/2023