PhD proposal

Study of redox-flow battery: characterization and design of an innovative Vanadium-Liquid-Solid cell

Host Laboratory : LEPMI, Grenoble
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Contact : florence.druart@grenoble-inp.fr
jonathan.deseure@grenoble-inp.fr

CONTEXT

Renewable energy sources require large-scale, stationary energy storage systems to balance out fluctuations in energy generation (6.5 GW from solar panel in France at 2015 and 8.5 GW from wind turbine in 2014, expected to exceed 20 GW at 2020) as well as to reduce the use of the fossil fuels and consequently to reduce the pollutant production as well as the CO_2 emissions. VSL (Vanadium-Liquid-Solid) project will advance the development of one of the most promising storage systems i.e. redox-flow batteries which concerns the conversion of "renewable" electrical energies in to chemical form (Fig.1 left) and the reverse process i.e. the recovery of the stored electrical energy (Fig.1 right). More precisely, the energy must be stored via a redox reaction into 'electroactive chemical compounds' present in solutions; these solutions are stored into high volume storage tanks (ST) and flow across electrochemical reactor (ER), the resulting system was named redox flow battery (Fig. 1).

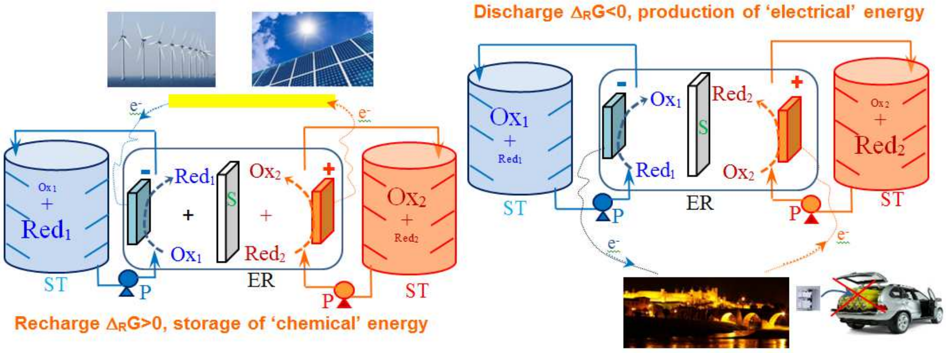

Figure 1: Schematic representation of the "conversion-storage-delivery energy" processes to study. ER: electrochemical reactor; ST: storage tank. P: pumps; S: separator. ($Ox_1/Red_1=V^{(III)}/V^{(II)}$ and $Ox_2/Red_2=V^{(V)}/V^{(IV)}$).

The project focuses specifically on the electrochemical reactor (ER, Fig.1) also called battery or generator. The redox systems involved in this project are vanadium salts (Vs):
at the negative electrode: $Ox_1/Red_1=V^{(III)}/V^{(II)}=V_2(SO_4)_3 \leftrightarrows VSO_4$
at the positive electrode: $Ox_2/Red_2=V^{(V)}/V^{(IV)}=(VO_2)_2SO_4 \leftrightarrows VOSO_4$.

The vanadium redox battery, so called 'all vanadium redox flow battery' was studied extensively by various authors, who use homogeneous liquid mixtures (dissolved salts) of the $V^{(III)}/V^{(II)}$ and $V^{(V)}/V^{(IV)}$). The battery is based on the following overall reaction:

$$V^{(IV)}+V^{(III)} \underset{\text{Discharge ; } \Delta_R G<0, \text{ recovery of electrical energy}}{\overset{\text{Recharge ; } \Delta_R G>0, \text{ storage of chemical energy}}{\rightleftarrows}} V^{(V)}+V^{(II)} \qquad \text{(R1)}$$

The VSL project, based on the knowledge acquired into the RFB “all-liquid-all-Vanadium/V-RFB” and the Semi-Solid lithium based RFB, introduces an entirely new (no works find bibliography) concept: “all-aqueous, all-Vanadium, Solid(crystalized V salts)-Liquid(dissolved V salts) Redox Flow Battery (VSL-RFB)”. It expects to overcome the limitations of the V-RFB (specifically ‘the low solubility->low stored energy ~40 kWh/m3), by “scientific” and “technological” actions enabling to :

i) bring new knowledge in the field,
ii) design, manufacture and optimize a VSL-RFB able to deliver 100 W.

The consortium was constituted considering that the material aspect for the VRFB is sufficiently treated (more than 100 papers found on the ‘all vanadium RFB’) and for VSL RFB it remains to study the aspects concerning: the electrochemical engineering, the fluid mechanics of the colloidal suspensions and the kinetics of Dissolution /Crystallization. It is constituted by 3 laboratories:

- Laboratory Navier (UMR 8205) brings skill in porous media rheology-Solid liquid flowing formulations
- Laboratory of the Chemical Engineering (LGC, UMR 5503) have an expertise in design and optimization of the electrochemical reactor and L⇆ S equilibria establishment, Modelling of the dissolution and growth rates
- Laboratoire d’électrochimie et Physico-chimie des Materiaux et des interfaces (LEPMI, UMR 5279) brings skill in multiphysic modelling, electrochemical characterization of cell and in membrane behavior and selection.

SUBJECT

Thesis is part of the subtask: Innovative technological actions for RFB-VLS design. It is divided in two parts:
(i) Experimental study of the 3-electrodes lab scale cell or single cell to study electrolyte behavior as well as membrane behavior.
(ii) 1D-model orthogonal of the flow axis and 2D-model that includes the hydrodynamics of the flow in the electrolytic compartments along the flow axis.

Experimental data of electrochemical characterization will be obtained using various electrochemical technics.
PhD candidate will study mass transfer in membrane and crossover in 3-electrodes lab scale cell. The aim is to select a membrane to separate both electrolytes of the battery; main required properties are i) to reduce the V cations cross-over, ii) to assure good mechanical and chemical resistance and iii) to cause ‘low’ Ohmic drop. All these experimental data will be completed with viscosity characteristic and solubility limits obtained respectively from the other partners. Then this data shall be implemented in models.

Hence, a multi-physical 1-D model (through the plane of the cell) will be developed taking into account the transport properties of the electrolyte and membrane; it will take into account transport phenomena in the electrolyte and the membrane as well as charge transfer kinetics. The 2-D model (or 3-D) will take into account a description of the flow distribution of both cell compartments, which is a key issue for this redox-flow technology. Based on the simulation, a sensitivity analysis of the cell design will be provided. From simulations, recommendations on residence time or velocity will assist the choice of flow rate or volume of the VSL-RFB compartments.

Hence, this Ph.D should bring scientific knowledge and also contribute to validate this technological concept.
-It will contribute to understand membrane behavior and crossover phenomena that play a crucial part in VSL-RFB performance.
-1D and 2D model will provide the theoretical approach to understand the current distribution into the electrolytic compartments,
-The screening of the effect of various operating parameters will help to its theoretical optimization of the battery minimizing the time consuming experimentations.