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Project coordinator name	Dr. Y. Álvarez Gallego
Project coordinator organisation name	Vlaamse Instelling for Technologisch Onderzoek (VITO)
Contact for queries:	yolanda.alvarezgallego@vito.be
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List of abbreviations

C-rate - Charge / discharge rate¹

CB - Carbon Black

CNPs - Carbon Nano Particles

DMC - Dimethyl carbonate,

DoD - depth of discharge²

EAM – Electro-active material

EAPs – Electro-active particles

EC – Ethylene carbonate

EIS – Electrochemical Impedance Spectroscopy

GITT - Galvanostatic Intermittent Titration Technique

LCO - LiCoO₂

LiNCM - LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂

LTO - Li₄Ti₅O₁₂

NaNM – Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O₂

PC – propylene carbonate

OCV – open circuit voltage

RES – renewable energy resources

RFB - redox flow batteries

SOC – state of charge³

SOD – state of discharge = DOD

SSFB - semi solid flow battery

VRB - vanadium redox battery

¹ Specifies the speed a battery is charged or discharged. The capacity of a battery is commonly rated at 1C, meaning that a fully charged battery rated at 1Ah should provide 1A for one hour. The same battery discharging at 0.5C should provide 500mA for two hours, and at 2C it delivers 2A for 30 minutes. A C-rate of 1C is also known as a one-hour discharge; 0.5C or C/2 is a two-hour discharge and 0.2C or C/5 is a 5-hour discharge.

² used to describe how deeply the battery is discharged. If we say a battery is 100% fully charged, it means the DOD of this battery is 0%, inverse of SOC (100% = empty; 0% = full); normally used when discussing the lifetime of the battery after repeated use

³ State of charge(SOC) is the equivalent of a fuel gauge for the battery pack in a battery electric vehicle (BEV), hybrid vehicle (HV), or plug-in hybrid electric vehicle (PHEV). The units of SOC are percentage points (0% = empty; 100% = full). normally used when discussing the current state of a battery in use

1 Final publishable summary report

The FP7 project INFLUENCE aimed to improve the fundamental understanding and control of interfaces of a battery type based on Li-ion and Na-ion active materials and redox flow battery systems: the semi solid flow battery (SSFB). The fact that the case study was SSFB set-up instead of a conventional Li-ion battery constitutes an asset, given that the methods and techniques developed are generic and could as well be implemented for conventional Li- and Na-ion systems (except the techniques addressing flow aspects).

The goal of the scientific activities of INFLUENCE was therefore to gain better insights into interface processes relevant to secondary batteries, taking as particular case study SSFBs. This entailed the examination of the following aspects:

- Formation of interfaces between the electrolyte and the Electro Active Particles (EAPs) in fluid electrodes.
- Colloidal interactions between EAPs and Carbon Nano Particles (CNPs), including the cross-interactions, as a function of electrode composition and state of charge.
- Interactions between fluid electrode and current collector, and their behaviour in the flow channels.

A lab scale prototype SSFB (ca.0.7 cm² surface area) was proposed and validated for the study these interactions. A variety of materials were evaluated as components for fluid electrodes; some of them were not commercial and have been optimized within the project (e.g. Na-ion EAPs, ionic liquid based electrolytes). Substantial efforts were dedicated to the optimisation of electrode formulation and its preparation.

Main project outcomes:

The scientific work provided the basis for the core technological goal of the project: to develop specific characterization tools for a reliable evaluation of interface processes (some of them generically applicable to batteries and supercapacitors):

- Battery analysis techniques were implemented to study the afore mentioned interfaces: EIS (Electrochemical Impedance Spectroscopy) and GITT (Galvanostatic Intermittent Titration Technique) were used to assess the effect of several parameters on the state of health of a SSFB.
- The safety of the system was evaluated by means of TGA-MS (Thermo-Gravimetric Analysis coupled with Mass Spectrometry).
- The rheological behaviour of the particles in fluid electrodes was first examined from the perspective of colloidal interactions between EAPs and CNPs.

- Rheological and electrical properties of the fluid electrode were investigated by means of electrochemical cycling experiments (charge/discharge) in a rheo-impedance set-up.

The project realised the first proof of concept for a non-aqueous SSFB based on the Na-ion chemistry, using P2-type $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ (NaNMC) and $\text{NaTi}_2(\text{PO}_4)_3$ (NTP) as positive and negative electrode, respectively. This concept opens the door for developing a new low-cost type of non-aqueous semi-solid flow batteries based on the rich chemistry of Na-ion intercalating compounds.

Experimental investigations have been complemented with computational modelling. At molecular level, a detailed kinetic mechanism was developed and validated for four material systems. At macroscopic level, the modelling of electrochemical cells in static and dynamic flow conditions was performed using COMSOL Multiphysics® various scales: laboratory cell (mono-channel), laboratory stack (single and multi-channel configurations) and larger electrochemical systems.

Conclusions from the modelling were crucial input for the design of a SSFB mini-stack (consisting of three cells connected in series, ca 70 cm² surface area), which was delivered and validated in the last months of the project, bringing SSFB energy storage systems to TRL 4.

Lastly, it was concluded from calculations that SSFBs electrochemical stack systems with power input/output up to 1 kW with a reasonable size (1.5 m x 1.5 m) could be feasible for energy storage and production at an household level.

2 Summary description of project context and objectives

The understanding and control of the SEI (solid electrode-electrolyte interface) in rechargeable batteries is of paramount importance from the point of view of performance and of safety. The physical and chemical phenomena occurring at these interfaces determine the kinetics of battery processes, and are key to the state-of-health and failure modes. Being able to monitor changes in SEI is therefore of particular relevance in order to control battery processes.

The FP7 project INFLUENCE aimed to improve the fundamental understanding and control of interfaces of a battery type based on Li-ion and Na-ion active materials and redox flow battery systems: the semi solid flow battery (SSFB). The fact that the case study was SSFB set-up instead of a conventional Li-ion battery constitutes an asset, given that the methods and techniques developed are generic and could as well be implemented for conventional Li- and Na-ion systems (except the techniques addressing flow aspects).

A flow battery is an energy system in which, at least, one of the electrolyte is pumped between the electrolyte tank and the electrochemical cell. The first redox flow batteries (RFB) were developed in the late 70s. Since then, a variety of flow battery systems have been proposed; among them, the all-vanadium redox battery (VRB) is an energy storage and conversion system currently used to store intermittent renewable energy as well as for stationary applications. Nevertheless, it suffers from low specific energy due to the limited solubility of vanadium in the used electrolytes. In 2011 researchers at MIT reported a new energy storage system named semi solid flow battery (SSFB). The SSFB is a promising energy storage technology that combines the flexibility in configuration and operation as well as independent scalability of energy and power capabilities of redox flow batteries with the high energy density of Li-ion battery materials

The operational principle of SSFB is based on RFB, but anolyte and catholyte consist of flowable suspensions of solid active materials instead of dissolved redox species, i.e. fluid electrodes. The chemistry of most reported SSFB relies on the chemistry of well-investigated Li-ion battery materials. A key aspect in both Li-ion and Na-ion batteries is the formation of the SEI when electrodes are operated outside the electrochemical stability window, due to reductive or oxidative decomposition of the carbonate based electrolyte. The formation of a stable solid electrolyte interphase (SEI), which is electrically insulating, at the negative electrode of conventional Li ion batteries has a positive impact in the functioning of the battery, making it possible to use active materials operating at very cathodic potentials, e.g. graphite at 0.1 V vs. Li/Li+. However, the fluid electrodes do not necessarily behave as conventional solid electrodes. There is a major difference between the SEI in Li-ion batteries and in SSFBs, namely: the location of the SEI. In classic Li-ion batteries, the SEI is formed around the “static” solid electrodes, allowing many contact points between particle/particle and particle/current collector to remain mostly “uncovered” for facile electron transport across the entire solid electrode. Thus, the SEI in Li-ion batteries is mostly located at the interface between electrode and electrolyte. On the other hand, in SSFBs the active particles are in continuous motion. The contacts for electron transfer between current collector and particles are severed and re-established continuously, which allows the SEI to cover the entire current collector. Thus, the SEI in SSFBs is mostly located between the current collector and the fluid electrode. Once the SEI is formed in SSFBs, the electrons must cross this electrically insulating barrier on their way from the current collector to the active material and vice versa. Whereas

the properties of the SEI in SSFBs may be very similar to those of SEI in a Li ion battery based on the same active material and electrolyte solution, the formation of SEI has a specific detrimental effect in the fluid electrodes of SSFBs since it hinders the electrical connection between the current collector and single particles dispersed in the electrolyte.

From an application point of view, the main differences and advantages of SSFBs with respect to conventional flow batteries are based on the fact that energy is stored in suspensions of solid storage formulations (the fluid electrodes). Charge transfer in the electrode is realised via dilute percolating networks of nanoscale conductors. This looks close to classic Li-ion and Na-ion batteries, except that the active materials flow through the cell. As for any of the secondary batteries known to date, fundamental insight in the interfacial processes is needed. Many processes in SSFBs are similar to 'classic' Li-ion batteries, e.g., the formation of a passive layer called SEI on the surface of e.g. anodic graphite. The addition of small graphite particles to the cathode material is needed at the cathode to enable electric pathways from the active material to the current collector; the use of the same type of carrier fluids (electrolyte) are used and finally, the active material particles which undergo the same type of stresses during the (de-) lithiation intercalation processes. In addition to interfacial aspects, there are also new phenomena to be understood:

- particles have to stay in suspension;
- the electric pathway connection is dynamic (breaking and formation of percolating structures);
- the current collector for lithium-ion chemistries it cannot be the graphite material (as it is in RFBs).

The primary goals of the project were:

- To study and optimize of interfaces developing between the electrolyte and the electrochemically active material particles in fluid electrodes. The acquired knowledge was subsequently applied to the chemical and morphological optimization of active materials as well as the design of optimized interfacial layers (also called artificial Solid Electrolyte Interfaces, art-SEI) capable of warranting stable interfaces.
- To improve the understanding and control the mechanical and conductive behaviours of the slurries. For this, it was a prerequisite to investigate the role of shape anisotropy and the nature (attractive or repulsive) of the short ranged interactions of the active materials besides the strength of the attractive forces for conductive nano-particles. The cross interaction should allow intimate contact between active material and the conductive particles.
- To complement experimental data with computational modelling in order to further improve the understanding of physical and electrochemical phenomena occurring at the interfaces at the microscopic scale, and to derive scaling rules towards macroscopic scale. This makes it possible to provide design recommendations leading to optimal interface behaviour (size of anodic and cathodic compartments, geometry of collectors, etc.).

One implicit objective for the period for the second half of the project was to implement the knowledge gained in the first half of the project for the design and realization of a SSFB stack by the end of the project.

The work was structured in four main areas of development: definition and design of the system, study of interface electrolyte/active material particles, study of interface current collector/slurry and modelling. The specific objectives for each of them is given in the corresponding subsection of the next section of the document.

3 Main S&T results/foregrounds

3.1 Definition and design of the system

The objectives of the activities on design and definition of the system were:

1. To define the demands on flow cells in electricity grid based applications;
2. Manufacturing of measurement cells for the interface analyses;
3. To select EAPs based on particle size influence and of surface modification effects;
4. To select a slurry with an optimum conductivity;
5. To select best candidate electrolytes.
6. Design of a stack and manufacturing of a cell based on recommendations from modelling results.
7. To validate methods proposed for the study of interfaces (electrolyte/active material particles and slurry/current collector) in an optimized semisolid flow cell. .

Objective 1 was addressed showing an overview of applications categorized according to the location in the electrical value chain ((generation, transmission and distribution and end-user) or according to their requirements (fast response, high power and high energy storage).

Based on previous experiences in redox flow batteries, Objective 2 was successfully addressed through designing a filter-press electrochemical cell in two configurations: half-cell and full-cell configuration. After that, according with all partners, this electrochemical cell was fabricated and validated by means of electrochemical test with slurry compositions using reference materials (i.e $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiCoO_2) in intermittent flow.

Objective 3 was explored testing a large variety of pre-selected active material particles dispersed in organic solvents with carbon black in both chemistries Lithium and Sodium ion. Based on the reversibility criteria that determine the performance of the active materials were selected the candidates. This concept is the percentage of charge that is reversible inserted/removed in/from the active materials and has been quantified by means of the coulombic efficiency. The negative electrode materials selected for semi solid flow batteries were ZnO, anatase TiO₂ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and positive electrode material were LiCoO_2 (LCO) and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LiNMC) for Li-ion chemistry. The negative materials were anatase TiO₂, together with $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ (NaNMC) for positive materials for Na-ion chemistry.

Objective 4 was addressed testing the electrochemical performances and electrical conductivity with two approaches:

- Improving the electrical conductivity of the electrochemical active particles of LTO with several surface treatments (i.e. thermal treatments in hydrogen and oxygen atmosphere). The slurry with superior performances was achieved with LTO hydrogenated.
- Varying carbon black concentrations ranging from 2 to 10 vol% in the slurry (since the viscosity of the solution was increased with carbon black content, no more quantity of carbon black was tested). The optimum electrical conductivity was obtained with slurries with slurry with major carbon content (i.e. 10%vol.).

Objective 5 was explored using several organic solvents (ethylene carbonate-dimethyl carbonate (1:1 in weight) in 1 M LiPF₆) and ionic liquids from Solvionic (Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR0408A) (1:9 in molar ratio) and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR1308A) (1:9 in molar ratio). The organic solvents are suitable for semi-solid flow batteries in Lithium and Sodium-ion battery. In the case of ionic liquid, alternative membranes to Celgard's separator have been tested obtaining little progress.

Objective 6 was accomplished: a mini-stack design was proposed at the end of 2015, with 3 cells of 12 cm long and 3 cm wide or 11 ml for the stack. The 3 cells in the stack are connected in parallel from a hydro-dynamical point of view, and in series from an electrical point of view. The stack was realized at VITO and delivered to IREC for validation.

For objective 7, a power cell was designed and validated using materials from the project, namely metal oxide from ECKART and ionic liquid from SOLVIONIC.

Main S/T results

In order to assess the future market of the application of semi-solid flow batteries (SSFB), an analysis of the requirements of energy storage devices for several services of the grid was carried out at the very beginning of the project. The basic role of an energy storage system is to absorb energy generated at one time and to discharge to supply at a later time. However, the choice of storage system for each application in the grid is strongly influenced by the required power rating and the duration for which it may need to continuously charge or discharge.

Among all energy storage applications, redox flow batteries (RFB) offer excellent versatility which has led this technology to become one of the most promising systems for application that requires intermediate values of power (typically 20 kW – 2 MW) and energy capacity (100 kWh – 8 MWh) and duration time of several hours (2-8 hours). Due to their similarity, RFB and semi-solid flow batteries (SSFB) are suitable for similar applications. The main difference between the two technologies is the higher energy density of the latter. This fact allows SSFB to occupy smaller volumes than other flow batteries to store the same amount of energy, and, thus, leading to a more compact system. Consequently, SSFB seem very suitable for applications in urbanized areas. SSFB can be deployed for integration of variable distributed generation, commercial and industrial energy/power management for which power requirements are in the range of 100-1000 kW and duration time of 2-10 hours. Table 1 summarizes the values of specific energy and energy density estimated for several SSFB chemistries.

Table 1: Estimated values for different semi-solid flow batteries

<i>Chemistry</i>	<i>Charge capacity / mAh g⁻¹</i>	<i>Cell voltage / V</i>	<i>Specific energy / Wh kg⁻¹</i>	<i>Energy density / Wh L⁻¹</i>	<i>Realistic energy density / Wh L⁻¹</i>
LTO	170	2,3	190 (105)	750 (250 [‡])	100*
LiNMC	160				
Al	1000	2,8	385 (190)	1590 (475 [‡])	190*
LiNMC	160				
Si	3500	3,6	550 (280)	2380 (715 [‡])	290*
LiNMC	160				
ZnO	660	2,0	230 (115)	1080 (325 [‡])	130*
NaNMC	140				

[‡] theoretical energy density for 30 vol% of active material in suspension

* energy density for 30 vol% of active material in suspension, reaching 50 % of the theoretical charge capacity, and achieving 80 % state of discharge.

Assuming non-ideal conditions, i.e. suspension containing 30 vol% of active materials, reaching 50 % of theoretical charge capacity of active materials and 80 % of state of charge, the energy density of semi-solid flow batteries vary between 100 – 300 Wh L⁻¹, which is in the order of 10-fold increase with respect to its all vanadium redox flow batteries. SSFB could cover several end applications such as integration of variable distributed generation, commercial and industrial energy/power management. In those cases, requirement varies from 100 -1000 kW and discharge time of 2-10 hours. For instance, the SSFB based on LTO – LCO, which is the chemistry with the lowest energy density, requires a volume of 10 m³ to store 1000 kWh, delivering a power of 250 kW in a period of 4 hours. On the other hand, values of 10 and 5mScm⁻¹ for ionic and electrical conductivity respectively, are considered acceptable to deliver good overall performances.

Based on IREC's experience in redox flow batteries, the first measuring cell prototypes for semi-solid flow batteries in the frame of the INFLUENCE project were fabricated based on a modular electrochemical cell design, in half-cell and full-cell configurations. The main advantage of such design is the high versatility which allows tuning of cell parameters by changing, adding or replacing only a few parts of the system. The half-cell configuration system was validated using a suspension containing LTO and Ketjenblack in intermittent flow. Reversible capacity values of ca. 140 mAh g⁻¹ were obtained together with low overpotentials /charge and discharge potential of ca. 1.70 V and 1.45 V, respectively) The full-cell configuration system was validated in intermittent flow using a suspension containing LTO plus Ketjenblack and LCO plus Ketjenblack as suspensions for negative and positive compartments, respectively. Based on the mass of the limiting suspension (LTO), reversible capacity values of ca. 100 mAh g⁻¹ were obtained with main charge and discharge potentials of ca. 2.8 V and 1.7 V, respectively. The measuring cell was validated as well under continuous flow of 3 mL min⁻¹, using a suspension containing LTO and Ketjenblack.

A number of candidate active materials were pre-selected and evaluated as candidate negative electrode material for semi-solid flow batteries: Si, SiC, Sn, Fe₂O₃, ZnO, Al, TiO₂ and Li₄Ti₅O₁₂ (for Li-ion

chemistry), and NaNMC, ZnO and TiO₂ (for Na-ion chemistry) Similarly, LiFePO₄, LiNMC and LiCoO₂ were evaluated as positive electrode materials for Li-ion chemistry, together with NaNMC for Na-ion chemistry. According to the selection criterion of electrochemical reversibility, from these materials we selected to be used as active material in the course of the project ZnO, TiO₂, LTO, LiFePO₄ (LFP), LiNMC and LCO for Li-ion chemistry and TiO₂ and NaNMC for Na-ion chemistry. However, at the mid-term review it was recommended to choose one single system, i.e. one combination of: active material for the positive electrode, active material for the negative electrode, conductive particles and electrolyte, and focus on that system during the second half of the project in order to ensure completion of the project plan and achievement of the major project objectives on time.

In the light of results obtained during the first half of the project, and the status of the research at Mid-Term, it was decided to focus on the better known Li-ion chemistry for the development of the SSFB mini-stack. The consortium therefore agreed in July 2015 on the following choice:

- LiNiMnCoO₂ (Li-NMC) as electroactive material for the positive electrode, i.e. cathode.
- Li₄Ti₅O₁₂ (LTO) as electroactive material for the negative electrode, i.e. anode.
- EC:DMC 1:1 wt/wt + LiPF₆ 1M (LP30) as electrolyte.
- Ketjenblack type KB600 as conductive material.

The formulation of fluidic electrodes contained at least 15% vol. particles of electroactive material (LiNMC for the cathode, LTO for the anode) and 10 to 15% volume of conductive particles (KB600). With this material system the maximum cell voltage is 2.7 V, and the nominal voltage for the single cell on discharge is 2V. The expected energy density is 50 W.h/l (specific energy 50 W.h/Kg), for 15 vol% of active material in suspension, reaching 50 % of the theoretical charge capacity, and achieving 80 % SoD. Notwithstanding the fact that the main line of development in the second half of the project focused on the Li-NMC / LTO system, some ongoing activities on NaNMC, on ZnO anode system and on ionic liquid based electrolyte were also completed.

Organic solvent, DC: DMC (1:1) in 1 M LiPF₆ from Solvionic, was selected and validated in semi-solid flow battery in both chemistry Li and Na-ion. Ionic liquid are not compatible with standard separator because of their higher viscosity, density and/or surface tension. Therefore, new separators compatible with the ionic liquids were required in order to be able to use ionic liquid based electrolytes. Alternative separators from nanofiltration applications have been tested with suspensions of ZnO, carbon black and ionic liquid based electrolyte from Solvionic, with positive results. These custom separators were only available at the end of the project.

Based on the experience made with the lab scale cell, it was decided that the stack had a very simple geometry consisting of thin parallel channels i.e. 4 mm wide channels were proposed. Therefore, it was proposed a stack of 3 cells of 12 cm long and 3 cm wide or 11 ml for the stack. The idea of using long channels leads to a higher flow speed and may result favourable against sedimentation. Also, it was decided to make the channel height of 1 mm or less since only the surface close to the current collector contributes to the reaction. The design of the stack was focused to maximize power output. In order to optimize stack design and performance, flow simulations were conducted in parallel to stack

construction to elucidate the best design. Comsol® was used to simulate the flow behaviour inside the stack. Several input were necessary for the flow model. These input values were the electrolyte behaviour obtained from viscosity measurements, particle sedimentation rate, the feasible amount of slurry that can be prepared by ball-milling, electrode over-potential and energy density measured by single cell and pressure, current collectors and pump considerations. Having in mind the results of the simulations, A 3 cell mini-stack design was proposed at the end of 2015. The 3 cells in the stack are connected in parallel from a hydro-dynamical point of view, and in series from an electrical point of view. The stack was realized at VITO and delivered to IREC for validation. The current collectors were divided in four segments along the flow path to increase the efficiency for SOC/DOD and to allow monitoring of each segment. A schematic representation of the final assembly and an exploded view of the stack are shown in figure 1.

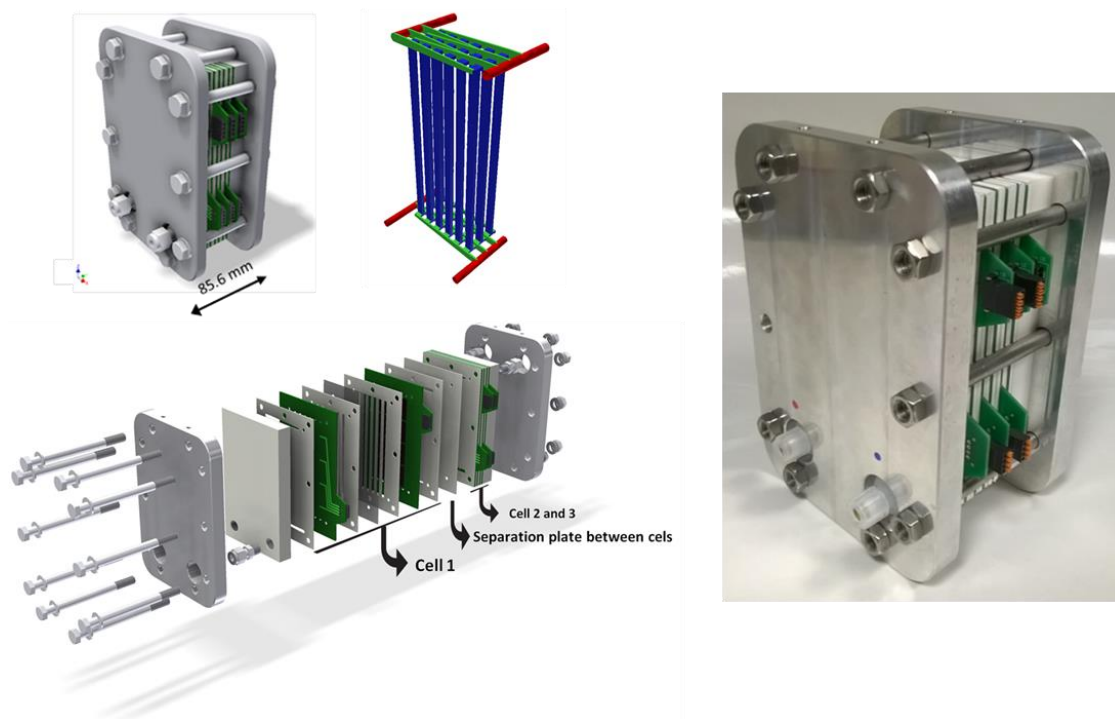


Figure 1: 3 cell stack: total assembly (top left), fluid compartments (top centre), exploded view (bottom left) and picture of the stack realised.

On February 2016, the stack manufactured by VITO was delivered to IREC in order to perform their validation (a second stack was delivered in June 2016). The system was tested in the glove box in order to avoid the contact with oxygen and water. The final pumping system used to flow the suspensions in and out of the cell was a peristaltic pump instead of the syringe pump in order to avoid the sedimentation within the stack. Prior any electrochemical test, the stack was filled with Dimethyl Carbonate (DMC) to detect any potential leaks, crossover or evaporation of the solvent. The suspensions compositions are described as follow:

- **negative electrolyte** : 15% Vol of LTO and 15% Vol of KB in 1M LiFP6 in EC:DMC 1:1
- **positive electrolyte** : 15% Vol of LNMC and 15% Vol of KB in 1M LiFP6 in EC:DMC 1:1

The system was tested in the glove box in order to avoid the contact with oxygen and water. The stack was first charged up to 10 % of the SOC and then overpotentials collected as a function of applied current density. Considering the voltages recorded during charge and OCV periods, the range of current densities that can be effectively applied in the system are in the range from 0.05-0.3 mA/cm² (0.5-3 A/m²), being the optimum values around 0.1-0.5 mA/cm² (1-2 A/m²), in order to avoid parasitic reactions and reduce the inefficiencies. These values of current densities are higher than those observed in a single cell due to the improved performance and higher electronic conductivity of the gold current collectors in comparison to other metals such as copper and titanium. The power capabilities of the stack are in the range of 10-60 W/m². The overall energy efficiency was however low. There is a clear need to improve the design of the system needs to be optimized in terms of flow and current distribution, while the main operational parameters such as the chemical composition and concentration of the electrolytes, the volume of the electrolytes, the flow rate and the current density need to be enhanced in order to observe an appropriate performance and energy efficiencies.

The implementation of the slurries based on 15% metal oxide nanoparticles (ECKART), graphene or carbon black and ionic liquid (SOLVIONIC) was carried out using the lab scale single cell. The poor reversible capacity is evident using carbon black at 1 mA and 3 mA of current intensity applied in static conditions, 8 and 3 mA h g⁻¹ respectively. This could be explained by two reasons: 1) low wettability of the separator Celgard 2500 and 2) low electrical conductivity. In order to overcome these issues a special separator was used as well as graphene additive in order to decrease the overpotential of the system. The first consequences of this approach were the slurry can be easily flowable up to 50 cycles of charge/discharge and a high reversible capacity (i.e. 1 mA was applied during 3h, we obtained a discharge at 1 mA during 2,25h) was obtained cycling the system at 1 mA, obtaining a coulombic efficiency ~70%.

The main conclusions from the study of the SSFB system were

- Design and validation of electrochemical cell with reference electrodes in half-cell and in full-cell configuration; fabrication and delivery of replicate prototypes for the study of interfaces. Reproducible values of reversible capacity were obtained using the electrochemical cell designed.
- Based on reversibility criterion, LFP, LiNMC, LCO and NaNMC were selected to be used as positive electrode materials, and ZnO, LTO and TiO₂ as negative electrode materials. The materials selected show a reversible capacity higher than 80% with high value of conversion in a single pass. Thermal treatment in hydrogen atmosphere and high carbon black contents in the slurry resulted in superior performance
- A proof-of-the concept for non-aqueous SSFB cell based on Na-ion chemistry was demonstrated for the first time. This first proof of principle has been achieved by employing P2-type NaNMC and NaTi₂(PO₄)₃ (NTP) as positive and negative electrode materials, respectively. The proposed battery stores 80 mAh g⁻¹ NaNCM within the voltage range of 2.2 V – 0.2 V.
- A three cell mini-stack design was proposed, constructed and validated . The 3 cells in stack are connected in parallel from the hydro-dynamical point of view, and in series from an electrical

point of view. The operation of the semi-solid flow battery under continuous flow conditions using peristaltic pumps in a multicell stack configuration is demonstrated for the first time.

- The use of an alternative separator (non-commercial) led to improved electrochemical performance with ionic liquid electrolyte system and metal oxide nanoparticles anode.

3.2 Interface electrolyte/active material particles

The main focus of this part of the project is the development of long-term stable interfaces between the active material particles and the electrolyte. This, of course, necessitates the identification of the most suitable analytical techniques for the ex-situ and in-situ investigation of the interface formation. Therefore, the identification and formulation of techniques was essential for the project, and was achieved.

The objectives of the work addressing the interface electrolyte/active material particles were:

1. To determine the role of the active material particles and the electrolytic system in the formation of long-term stable SEIs;
2. To elucidate the role of the morphology of electrochemically active particles on interfacial phenomena;
3. To characterise and optimise the interfaces between the electrolyte and the electrochemically active material particles in fluid electrodes;
4. To elucidate the impact of the solvent and SEI forming additives on the characteristics of the interface between electrolyte and active material;
5. To investigate the safety of the system;
6. To develop in-situ monitoring of the State of Health of SSFBs with the scope of achieving in-line controlling of the interfaces to prolong their operative life.

The electrochemical performance and structural/morphological properties of the various pristine active materials to be used in the Li- and Na-based systems was intensively investigated and optimized (Objective 2). This, of course, is interconnected to the objective of identifying the influence of the active material, the particle properties as well as the electrolyte, on the active material/electrolyte interface (Objective 1, Objective 3). The investigation of the influence of the active material resulted in the successful selection of electro-active particles (LiNCM, LTO, ZnO for the Li-based system and NaNCM, LTO, anatase for the Na-based system) with preferentially spherical particle morphology and nano particle size in 1M LiPF₆ in EC:DMC = 1: 1 and 1M NaPF₆ in EC: PC = 1:1 as electrolytic solution for the Li- and Na-based system, respectively. This facilitated the formulation of optimized fluid electrodes with optimized solid electrolyte interface allowing facile ion diffusion (Objective 6). Optimization of the fluid electrode composition (i.e. conductive agent content, effect of electrolyte additive soon planned) was continued throughout the project and targeted an enhancement of electronic and ionic conductivity .

In-situ techniques to investigate the evolution of interfaces in fluid electrodes were defined, which was important for Objective 5. In detail, electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) were found to be suitable techniques which can reveal the effect of several parameter on the state of health of a SSFB. Objective 4 was achieved performing a detailed thermogravimetric analysis (coupled with mass spectrometry). It was concluded from ex-situ investigations that the presence of the SEI to be detrimental for the fluid electrode performance. The reason is the electron insulating nature of the cathodic and anodic SEI which lead to a strongly decreased electrochemical performance (Objective 1 and 2). Nevertheless, it should be also highlighted that the target of developing optimized artificial and long-term stable interfaces could not be fully attained. However, the work carried out provide the main reasons of failure and the most promising future directions for the improvement and optimization of SSFBs.

Main S/T results

The investigation of the solid/ liquid interface in fluid electrodes was first performed ex-situ via the use of solid electrodes to facilitate the identification of the most suitable techniques and the material optimization. Different analytical techniques were used in dependence of the specific properties of the material in order to enable a fast and facile optimization. As a consequence of the optimization process using various analytical techniques, promising techniques for the characterization of the solid-liquid interphase could be identified. Various materials ($\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ (NaNCM), anatase TiO_2 , ZnO (provided and optimized by ECKART), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (lithium titanate, LTO)) have been tested and characterized structurally and electrochemically in combination with different electrolytic solutions provided by SOLVIONIC. Substantial efforts were dedicated to the study of non-commercial materials: NaNCM (cathode material for the sodium based system, developed at KIT), as well as Al flakes and ZnO particles (ECKART). The active materials were optimized and characterized at KIT via the use of various analytical techniques, simultaneously proving their capability for the ex-situ characterization of the active material electrolyte interface, and provided to the project partners upon request. NaNCM and anatase materials revealed a very good electrochemical performance, superior to most of related materials in literature. The cycling performance of anatase reveals one of the best high-rate long-term cycling performance reported so far. Electronic conductivity was identified as limiting factor for the performance of these fluid electrodes, revealing that an optimization of electrode composition is crucial to enable improved performances and will be the focus of future activities.

LiNCM and LTO based fluid electrodes were studied extensively in the second period of the project, paying special attention to the influence of the state of charge (SOC) as well as the storage capability of the fluid electrodes (with respect to possible ageing phenomena). These properties were considered fundamental in order to allow the formulation of optimized fluid electrodes and the investigation of their properties. It could be revealed that the stability limit of the electrolyte determines the properties of fluid electrodes as evidenced via the ex-situ characterization via XRD, SEM, EDX and TEM. After various experiments it was concluded that the formation of the electronically insulating SEI layer on the active material particles - as a result of the reductive electrolyte decomposition below 1.0 V – is the main reason for the poor electrochemical performance. This issue represents a tremendous challenge for the negative electrodes. However, the use of active materials at voltages below 1.0 V would enable higher energies and improved electrochemical performance which is why more detailed investigations are surely interesting. For the positive electrode the upper cut-off voltage upon charge and oxidative

stability of the organic electrolyte were the most important criteria. The cut-off voltage of 4.6 V found for LiNCM indicated structural degradation. It should be highlighted that the electrochemical stability window for fluid electrodes is narrower with respect to what is known for conventional batteries with solid electrodes. This is, most probably, related to inhomogeneities in the fluid electrode (e.g. local difference of the conductive carbon content) which leads to inhomogeneous current distribution).

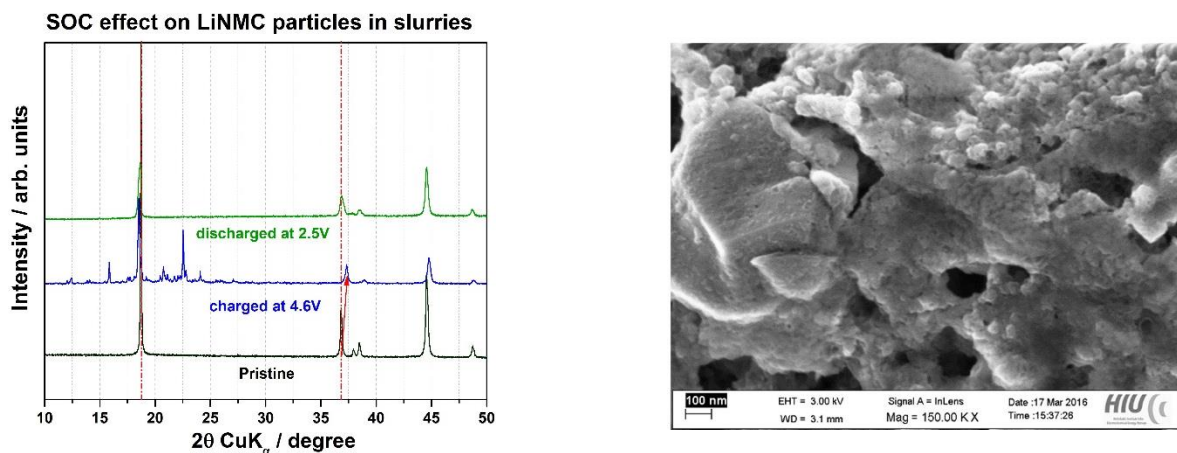


Figure 2: X-ray diffraction patterns of the pristine, charged (4.6 V) and discharged (2.5 V) (left) and SEM image (right) of the fully charged LiNCM (4.6 V) from the separated solid content of corresponding fluid electrodes.

Fluid electrodes were stable upon short-storage (e.g., up to one week) but not for long-term storage (e.g., after one month). This was evidenced via SEM and EDX by the formation of a passivating film on particles of LiNCM. Finally, it should be noted that the sealing of the cell is an important requirement as a strongly increased reactivity for fully charged and long-term stored materials is observed which restricts their use or handling in ambient air atmosphere.

All active materials have been investigated in fluid electrodes. Anatase TiO_2 and LTO have been tested as anode material in sodium-based fluid electrodes. Of particular interest was their electrochemical performance as they operate outside of the electrochemical stability window of the electrolyte and, thus, form a solid electrolyte interphase (SEI), which is known to decrease the electronic conductivity. In fact, both materials did not reveal suitable performance in fluid electrodes which is mainly due to the SEI formation. Most important, thus, is the further optimization of the fluid electrode composition, i.e. conductive carbon content, in order to optimize the ionic and, especially, electronic conductivities.

Nevertheless, it was successfully demonstrated (in collaboration with IREC) that non-aqueous SSFBs could operate on Na-ion based chemistry. This first proof of principle has been achieved by employing P2-type $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ and $\text{NaTi}_2(\text{PO}_4)_3$ as positive and negative electrode materials, respectively. In fact, this example illustrates that the low conductivity of the fluid electrode (due to SEI formation) can be mitigated by using a negative electrode material that operates within the electrochemical stability window of the electrolyte. The proposed battery stores 80 mAh g^{-1} NaNCM within the voltage range of 2.2 V – 0.2 V. First results are encouraging but certainly indicate the need for a better understanding and control of irreversible charge losses in this type of battery. A proper selection and optimization of the

electrolyte, active materials as well as cycling conditions, will certainly result in a significantly improved electrochemical performance.

For slurries based on the Li chemistry, the effect of the conductive carbon content on the conductivity of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LiNCM) and LTO was investigated via electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge tests. This is of particular interest for improved understanding of the solid electrolyte interphase and for enabling improved electrochemical performances of the fluid electrodes. In fact, slurries containing Li-ion electrode materials with optimized conductive agent content (at least about 10vol%) revealed a good electrochemical performance, e.g., 120 mAh g^{-1} at C/10 for LiNCM electrode and 25 mAhg^{-1} at high current rates of C/3 for LTO. Results revealed that electrochemical impedance spectroscopy is the right and promising method for the optimization of the fluid electrodes, which is necessary to enable a good performance of, e.g., the negative fluid electrodes for the sodium-based system.

As a strategy to improve electrochemical performance of the electrodes metal oxide coatings (to improve the stability of the interface and the structural stability) and carbon coatings (to enhance the electronic conductivity) were carried out on the different selected active materials for the lithium and sodium based system. For some materials an extraordinary electrochemical performance could be achieved in conventional solid battery electrodes (e.g., electrochemical performance of carbon coated anatase TiO_2). Nevertheless, in fluid electrodes the formation of the electronically insulating SEI decreases the electrochemical performance. This hinders the use of an active materials outside of the stability window of the electrolyte and results clearly indicate that this limit represents a tremendous challenge for SSFBs.

The evolution of the SEI was studied as well upon cycling and upon storage for LiNCM based fluid electrodes via XPS, in order to develop strategies to improve the electrochemical performance of fluid electrodes. XPS spectra indicated the presence of Li_2CO_3 , LiOH , LiF , LiPF_6 , $\text{PF}_5\text{-}2\text{xOx}$ and ethylene carbonate on the particle surface for all samples. These compounds derive from the fluid electrode composition, the reaction of LiPF_6 with moisture and HF as well as the ageing of LiNCM in ambient atmosphere.

The development of long-term stable interfaces between EAPs and the electrolyte was one of the core topics of the project. The identification and formulation of the most suitable techniques for the ex-situ and in-situ investigation of interface formation was essential in the first period of the project. Galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) were identified as most promising techniques and can provide correlating results about the state-of health and might also allow for in-line controlling of SSFBs. Especially EIS is able to reveal changing properties of the fluid electrode (nature of active material, conductive carbon content, active material particle conductive carbon network) as well as the cell components (i.e. current collector) or cell dimensions (i.e. channel size). The effect of several parameters, e.g., temperature, pre-shear, conductive carbon content in the fluid electrode, state of charge/discharge of the fluid electrode, the specific active material as well as the current collector, on the impedance spectra could be revealed. The state of health of a SSFB was found to be mostly affected by parameters that influence the sensitive particle network. This result provides important information in order to achieve the in-operando controlling of SSFBs. The polarization of the electrode can be an indicator for the state of health of a fluid electrode. In

general, a lower cyclability of the fluid electrodes is observed if a higher polarization than 0.4 V is detected. Once the polarisation is higher than this threshold counter strategies (i.e. changing the current, flow rate, temperature or composition of the fluid electrode) need to be undertaken in order to prolong the cycle life of SSFBs.

The thermal resistance of the system was evaluated by means of TGA (coupled with MS). The thermal behavior of the related fluid electrodes is determined by the electrolyte. All materials exhibited enough thermal resistance for the use in SSFBs, as they only release minor quantities of oxygen at temperatures as high as 600 °C. However, thermal analysis revealed a higher stability for LiNCM and LTO compared to the active materials of the Na-based system which can be interconnected with the morphological properties and suggests lithium-based SSFBs to be more suitable for application and upscaling. The thermal behavior of the related fluid electrodes is determined by the electrolyte. Temperatures beyond 100 °C should be avoided in order to prevent the rapid evaporation of the electrolyte solvents. DSC measurements reveal that 5 °C is the lowest operating temperature for the Na-based system and 5 °C for the Li-based system. Furthermore, the thermochemical properties of aged LTO- and LiNCM based fluid electrodes (stored for different time or cycled to a different state of charge) have been investigated. In addition, also the thermal chemical behaviour of pristine electrodes in presence with inert cell components (current collector, separator) as well as the effect of material crossover (mixing of the positive and negative electrode) was evaluated. Storage time, cell components (current collectors, separator) and material crossover were found to have a low impact on the thermochemical properties. In contrast (and in accordance with previous investigations), the state of charge has a stronger impact on the thermal properties and can lead to different thermochemical properties of a SSFB.

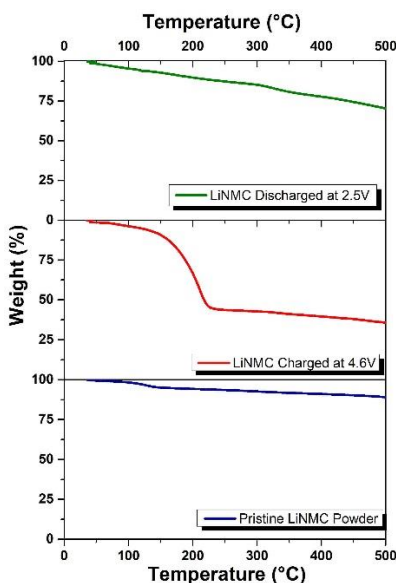


Figure 3: TGA-MS results for the separated solid components of pristine, fully charged (4.6 V) and fully discharged (2.5 V) fluid electrode of LiNCM.

The main conclusions from the study of the interface electrolyte/active material particles were:

- Advancement in the knowledge of Na-ion batteries. NaNCM, a novel layered P2/P3 oxide cathode materials containing four different metals (Mn, Ni, Fe and Mg) were synthesized via a solid state process. The synthesis was optimized and upscaled (up to 20 g per batch). NaNCM

was also demonstrated for the first time as active cathode material in non-aqueous SSFBs, with a storage capacity of 80 mAh g^{-1} NaNCM within the voltage range of $2.2 \text{ V} - 0.2 \text{ V}$.

- Various techniques successfully implemented for ex-situ investigation of interfaces ion fluid electrodes, including X-ray diffraction, scanning/transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, electrochemical impedance spectroscopy, chronopotentiometry, cyclic voltammetry, galvanostatic intermittent titration technique.
- Identification and implementation of analytical techniques for in-situ characterization of interfaces in fluid electrodes: electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT). While the former technique gives indication for the limiting processes (e.g. ionic or electronic conductivity, charge transfer resistance, formation of passive layer) the latter technique is able to indicate the state of charge/discharge (e.g. via comparing the open circuit voltage of fluid and solid electrodes) for the semi-solid flow battery.
- The impact of the solvent and SEI forming additives on the characteristics of the interface between electrolyte and active material was clarified, finding out a clear indication that the presence of the SEI results detrimental for the fluid electrode performance, mostly due to its insulating nature.
- Very good progress was achieved in the understanding of SEI formation and characteristics in fluid electrodes. Nevertheless, the target of developing optimized artificial and long-term stable interfaces could not be reached. However, we could provide the main reasons of failure and the most promising future directions for optimization of SSFBs.
- Optimization of the fluid electrode composition (i.e. conductive agent content, effect of electrolyte additive soon planned) was continued throughout the project and targeted an enhancement of electronic and ionic conductivity

3.3 Interface current collector / slurry

The interface current collector/slurry was investigated based on rheological and conductive characterisation of candidate slurries. Two particle components are needed in the slurries for SSFB: Electro Active Particles (EAPs) for storage of electrochemical energy, and Carbon Nano Particles (CNPs) for conducting the electrons to and from the current collectors. The objectives of the activities addressing the interface slurry/current collector were:

1. To understand how the electrode slurries flow inside the battery;
2. To understand transport of current to collectors, before and after electrochemical cycling;
3. To optimise fluid formulation and filling strategy.

Objective 1 was first addressed through study of particles interactions, rheology and visualization experiments. It was found that the network formed by the Carbon Black (minority particulate component) dominates the rheological response: a gelled state (with micron-scale hetero-geneties) at

rest, and a weakly aggregated fluid under shear. While some EAPs (NaNCM, TiO₂) appear to be aggregated as well, this aggregation is much weaker. Hetero-interactions between the EAPs (NaNCM, TiO₂) and CB appear to be relatively weak. All fluids with compositions pertinent to SSFBs behave like a gel at rest and strongly shear thinning in flow. Both behaviours should be of importance for the operation of SSFBs. Rheological experiments on KB were extended to get a better understanding of the effect of prolonged shear flow on i) the viscosity curve and ii) the yield stress. It was found that the (globally shear thinning) viscosity is determined by two reversible processes: a fast one which was attributed to the making and breaking of individual bonds between KB units, and a much slower one which could be due to (dis)entanglements inside aggregates. Cessation of flow resulted in a yield stress that also depended on the shear rate and its duration. This picture is consistent with an almost instantaneous sticking and consolidation of the aggregates in a network structure.

Also mixtures of 1 wt% KB and EAP (LiNCM or LTO) were studied for their rheology. Adding EAPs (up to 7.5 wt%) always resulted in higher viscosities, from a factor 2 at 1000/s to a factor 10 at 0.1/s. The effects of electrochemical cycling (up to 4 half-cycles) on the viscosity curves were found to be significant. For KB+LiNCM the changes induced by charging seem reversible, with the low-voltage state corresponding to a 2-5 times higher viscosity and yield stress. For KB+LTO the viscosity and yield stress was found to be lower in the low voltage state, but with a superimposed trend which decreases these quantities also with half-cycle number. Reductions up to a factor 7 were found. Computer simulations at UCAM were extended to rods, formed of a chain of two types of particles. The particles at the end attracted other end particles. All other interactions were purely repulsive. Repulsion of the particles in the middle of the rods was necessary to avoid bundle formation. The system was modelled with Langevin dynamics using the HOOMDB-blue software package. Starting from a regular arrangement of rods, the particles assembled into a percolating network with no obvious crystal structure. The parameters were chosen to give a percolating network at a volume fraction of 0.6%.

Objective 2 was addressed for fluids before electrochemical cycling. After observing the large heterogeneity of the CB network and unfavourable signal-to-noise ratios at low frequencies (corresponding to small length scales), experiments on chip were discontinued and a rheometer based Electrical Impedance Spectroscopy (EIS) was developed in house. Measurements at rest and under shear flow indicated a strongly concentration dependent electron conductivity, and showed that this ability is reduced in shear flow, and also in the presence of (much more abundant) EAPs. Electrochemical cycling experiments were performed at UNIVERSITEIT TWENTE in the rheo-impedance setup after modification of the latter. In subsequent (dis)charging steps at 1.5 mA (estimated C-rate: C/5) the capacity of both KB-EAP mixtures was found to diminish appreciably (about a factor 3). Measurements of the electrical impedance per step indicated modest changes (up to a factor 2) in electronic resistance in case of KB-LiNCM (cycled between 2.5 and 4.5 V vs Li/Li⁺) but a drastic increase in resistance after 1 cycle for KB-LTO (cycled between 1.0 and 2.5 V). This is very likely due to SEI formation. Transport phenomena in Semi Solid Flow batteries (SSFB) were investigated by IREC by the use of Electrochemical Impedance Spectroscopy (EIS). From the various impedance contributions observed in a SSFB, the interphase between the current collector and the semi solid suspension is the most resistive one. Its capacitive and resistive components are determined by the conductive additive e.g. Ketjenblack or activated carbon. A contact resistance model for SSFB has been proposed.

Steps towards objective 3 were pursued by experiments at UNIVERSITEIT TWENTE in consultation with VITO. Fluid formulation was explored by variation of the CB content and the EAP content for a few systems. Concentrations were reached (e.g. 30 wt % TiO₂) where the slurry does not flow any-more like a continuum. The conductivity of the static CB network was found to depend on the shear rate applied before the rest state. This implies that flow rates and wall-slip during filling of the SSFB may significantly affect the performance of the SSFB. Flow curves measured in Twente were used as a basis for design of the flow geometry by VITO (in WP2). One aspect of chemical formulation is the order in which the components (KB, EAP, solvent, salt) are mixed. Rather than studying this empirically, UNIVERSITEIT TWENTE investigated for each of the interactions (KB-KB, KB-EAP and EAP-EAP) under which salt conditions they are attractive. If attractions could be 'switched on' independently via the salt concentration, then this could allow a better control over the self-assembly of the particle network. Flocculation tests and rheology indicated that neither LiNCM nor LTO shows significant self-aggregation at any salt concentration. The reason for this (favourable) behaviour was not investigated in depth. KB flocculates under nearly all conditions; with an apparent activation energy barrier in absence of salt. At this condition, aggregation is found between KB-LTO and between KB-LiNCM. At 1 M salt both mixtures appear to hetero-aggregate as well, although the proof for this is less sound in case of LiNCM. If hetero-aggregation cannot be avoided, then most likely a randomly mixed network will result.

Main S/T results

Two EAP systems, Al and ZnO, were developed and delivered by ECKART. In consultation with partners, the work on Al particles was put on hold already in the initial months of the project due to unsatisfactory electrochemical performance. In the developments on ZnO particles, a transfer to ionic liquid was made possible using isopropanol as intermediate liquid. Also the preparation and dispersion of ultrafine graphite was explored. Work was also done to improve the stability of these dispersions in ionic liquid. Colloidal interactions can only be studied for (sub)micron sized particles. NaNCM consisted mainly of larger particles, necessitating the use of only the small dispersible fraction, or the use of milling. Use of planetary ball mills was explored. Generally, a reduction in size was achieved; the particle interactions will be analysed. Ketjen Black 600 and two TiO₂ systems were already colloidal from the start. SEM and DLS experiments showed that they consist of smaller sub particles that are permanently bonded. This makes a description of their interactions more complex than for homogeneous spheres as assumed in standard theories. We found that KB 600, anatase TiO₂ and NaNMC particles all have a tendency to aggregate in carbonate solvent with 1 M salt. Very dilute systems were explored for studying particle pair interactions. In this regime, formation of aggregates is relatively slow and measurable via the growth of the aggregate size and (the speed of) particle settling. Increase of the salt concentration from 0 to 1 M revealed increases in flocculation rate, suggesting that colloidal stability is determined by a balance between (salt dependent) electrostatic repulsion and Van der Waals attraction. Also the stability of KB at the (much higher) concentrations relevant to SSFBs was explored. Here it was found that even in absence of added salt, the particles tend to aggregate. This apparent contradiction with the observations at lower KB concentration might be due to a combination of very weak aggregation and the spatial distribution of sub-units inside the KB.

ECKART developed slurry systems that offer high colloidal stability. Metal oxide dispersions were prepared with optimum particle shape and size. Stabilizers were identified and used to prevent reaggregation of ground particles. Milling experiments were performed in isopropanol, which

represents an appropriate transfer solvent for dispersing particles in ionic liquids (for SSFBs). Particle size and shape were analyzed via light scattering and electron microscopy. Stability of the dispersion was evaluated via spectroscopic measurements. Several (meta)stable suspensions of metal oxide (at 14 wt%) in Pyr14TFSI ionic liquid (from Solvionic) were obtained. To create electrically conductive additives, at ECKART both graphite and graphene were successfully dispersed together with the metal oxide particles in the Ionic Liquid.

In the second period of the project UNIVERSITEIT TWENTE extended their study of colloidal interactions, focusing on KB, LiNCM and LTO in EC:DMC solvent (as recommended during MT review). Systematic variations of the (LiPF₆ and LiTFSI) salt concentration (from 0.0 to 1.0 M) were made to disentangle the different contributions to the particle pair interaction. Increasing the salt content, a remarkable inversion of the zeta potential (from negative to positive) was found; suggesting preferred adsorption of Li⁺ by the KB particles. The second effect of adding more salt was an enhanced screening of the electrostatic repulsion, leading to a loss of colloidal stability under battery fluid conditions. A follow-up work by UNIVERSITEIT TWENTE was focused on the interactions in (dilute) binary particle mixtures: KB+LiNCM and KB+LTO. Dynamic Light Scattering and zeta potential measurements showed that, remarkably, LiNCM and LTO do not significantly self-aggregate at any LiPF₆ concentration. In absence of salt, only hetero-aggregation between (negative) KB and (positive) LiNCM or LTO takes place. The -for SSFBs more relevant- behaviour at high salt content, required a more careful analysis since here also a rapid KB-KB aggregation takes place. From optical turbidity measurements it could eventually be concluded that LTO aggregates with KB.

Initial experiments were performed at UNIVERSITEIT TWENTE in a microfluidic chip (developed in house) and EIS measurements, but this strategy was not satisfactory for the evaluation of the slurries. As an alternative, an extension of the rheometer was built. Electrical isolation between the top and bottom plates, improved electrical shielding and the use of Hg in the vapour lock, allowed measuring the electrical impedance between surfaces separated by an adjustable gap, as a function of shear rate. An advantage is that these electrical properties are measured in conjunction to the mechanical properties of the very same fluid. Experiments with KB600 in carbonate solvent with 1 M salt showed that the conductance is highest in the quiescent state. Shear flow results in lower conductance, in accordance with the picture of a network that breaks up. Importantly, the conductance at rest was found to depend on the previously applied shear rate. This could have implications for the optimum filling protocol of the SSFB. Presence of TiO₂ in relatively large proportion resulted in a lower electronic conductance, suggesting a perturbation of the CB network.

Since the electron conductivity mainly originates from the KB, suspensions of 1wt % KB alone in EC:DMC + 1 M LiPF₆ were studied in depth for the influence of mechanical shear history. In the flow regime (at shear rates 100-1000 /s), a stepwise change in shear rate was found to cause two responses in the conductivity: an instantaneous one, plus a secondary one which was much slower but also stronger than (i.e. overcompensating) the first one. In the quiescent state, the electron conductivity depends on the magnitude and duration of the preceding shear rate. These behaviours (with implications for optimum mechanical formulation of SSFBs) were interpreted with a model in which KB units aggregate into fractal structures, with a size and density that depends on the shear rate (history). The conductivity of the ensemble is determined by the number density of conductive pathways. In flow, these pathways get interrupted but if the gap between aggregates remains in the nm range then tunnelling can still provide

conductivity. This was described with ‘effective medium’ theory. The model fits to the measured data are in agreement with a picture where (after a change in shear) not only instantaneous breakup of (or sticking between) aggregates takes place, but also slow (dis-) entanglements within the aggregates.

Several fluids were studied with rheometry. Both the quiescent state and flow (at variable rate) situations were addressed, to match the scenarios during filling, emptying and optional stirring. Suspensions of KB600 in carbonates plus 1 M salt showed a consistent behaviour. At rest the particles form a gel; i.e. a dominant and frequency-independent storage modulus $G'(\omega)$. Its magnitude strongly increases with the concentration of KB600 (varied from 0.1 to 2.0 weight %). In flow the viscosity strongly decreases with shear rate, following an exponent of -0.8 to -0.9. The magnitude of the viscosity at a given shear rate scales similarly with KB concentration as the storage modulus. Also measurements were made of the (yield) stress required to make the material flow continuously. Also this quantity scaled roughly in the same way with the KB concentration, indicating that the critical strain (the brittleness) does not vary much. All these observations clearly point out that the rheology of KB in carbonate solvent can be tuned via the concentration.

The rheology of EAPs in the same continuous phase liquid was studied at a concentration of 15% (by weight) for one NaNMC and two TiO_2 systems. At this typical concentration, all materials showed liquid-like behaviour, i.e. no measurable storage modulus or yield stress. Accordingly, we also found that these fluids are not able to completely withstand gravity. The flow curves showed either a constant viscosity or a weak shear-thinning, indicating that the EAPs form either stable or very weakly aggregated systems.

Mixtures of 1% KB and 15% (by weight) EAP show a similar rheological signature as the KB suspensions, in spite of the relatively low abundance of the KB. The magnitude of the mechanical resistance c.q. rheological response is enhanced by the presence of EAPs, to an extent that varies per system: a factor 2-10. Unlike the EAP suspensions without KB, the mixed systems do not show a noticeable particle settling. It appears that the yield stress provided by the KB network is large enough to keep the EAPs homogeneously dispersed. Similar observations (by partners) for systems with larger (micron range) EAPs suggest that this functionality of the KB is generic. Experiments with a confocal scanning laser microscope using macroscopic or microfluidic cells with thin transparent walls allowed a certain visualization of materials at rest and in flow (time-resolved at 100X magnification, Figure 4).

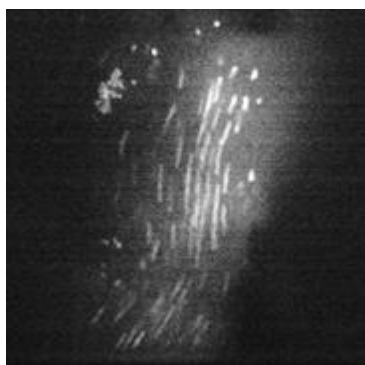


Figure 4: Snapshot of liquid flow (from top to bottom) in a mixture of 2% (w/w) KB 600 in EC:DMC in a micro channel, as visualized by a small fraction of (surfactant stabilized) fluorescent silica spheres.

In absence of EAPs, aggregates and networks of KB600 in carbonate solvent could be visualized in situ, albeit indirectly by using added fluorescent tracer particles. These particles explore the free liquid via diffusion, but on encounters with a KB network they can also stick to (and decorate) the latter. First experiments in micro-channels indicated the presence of large $O(10 \mu\text{m})$ clusters of KB which were firmly attached to the glass wall. As such they precluded the formation of regular flow patterns at this length scale ; flow visualization experiments showed flow through a porous network.

The measurements of electrical impedance at UNIVERSITEIT TWENTE were done in conjunction to a study of the rheological behaviour. Subjecting the KB fluid to a step in shear rate, also a two-stage response in the viscosity was observed. In(de)creasing the shear leads to an instantaneous de(in)crease in the viscosity, followed by a slower change in the opposite direction. However unlike with the conductivity signal, the secondary response in the viscosity was only minor (no overcompensation). The dependence of the viscosity on mechanical (pre-shear) history implies that at the microscopic level, the structure of the aggregated KB ensemble is also history dependent. The broadly accepted model of fractal aggregation (implying that more total solvent volume gets immobilized as the aggregates get bigger) was used to account for the shear-rate dependent viscosity. It was combined with the aforementioned 'effective medium' approach to corroborate the picture of aggregates that grow but also densify (entangle) after a reduction in shear rate. Cessation of shear resulted in fast transition of the fluid into a gel, with a storage modulus and yield stress that depended on the preshear history. The calculations of aggregation behaviour at UCAM showed that the main control is the length of the rod: a longer rod gives a percolating network at a lower volume fraction. The parameters require further tuning to increase the efficiency of assembly. Currently work is in progress to establish the correct combination of parameters that would lead to the most efficient percolation. Another avenue of further exploration would be to see how percolation depends on the nature of the carbon black used. Larger particles, which had a purely repulsive interaction with each other and the rods, were introduced to represent the nanoparticles. It was still possible for a network of Ketjen black to form, with the nanoparticles in the cavities of the framework. Going forward we intend to use Dissipative Particle Dynamics to model the viscosity of the network as a function of shear flow.

At UNIVERSITEIT TWENTE, a custom rheometer adaptation was developed to study rheological and electrical properties of fluid electrodes 'in situ' while the fluid is electrochemically cycled. Suspensions of only KB and KB+EAP in EC:DMC + 1 M LiPF₆ were studied. For KB+LiNCM fluid electrodes, the electronic conductivity and mechanical impedance were found to be functions of the state of charge, with higher voltage states versus Li/Li⁺ resulting in larger values of the aforementioned properties. This effect was found to be reversible over multiple cycles. The Coulombic efficiency of cycling however was found to be low. For KB+LTO fluid electrodes, the electronic conductivity and mechanical impedance were found to be functions of both the state of charge and cycling history. Higher voltage states versus Li/Li⁺ resulted in larger values of the aforementioned properties, however previous cycles had an additional irreversible effect. This irreversible effect reduced the mechanical impedance and drastically reduced the conductivity with increasing cycle count. The Coulombic efficiency of cycling was also found to be low. Reference experiments with only KB fluid demonstrated the same trends as the KB+LTO fluid electrodes. These effects are thought to be caused by the formation of SEI.

In order to investigate the interface degradation between current collector and slurry, a special electrochemical cell was designed and developed. The design of the electrochemical cell consists in the

same structure filter-press developed in the WP2 with several extractable pieces of the aluminium and copper current collector. Using these extractable current collectors, we can obtain information about their degradation in several times of the electrochemical test by means of their ex-situ analysis (i.e. XPS, HRTEM, SEM ...). Parallel, similar analysis will be carried out with the slurry in order to correlate the results. Moreover, the diffusion processes were investigated using this experimental set-up. The bulk conductivity of LTO and LNCM has been measured by conventional AC impedance. LiNCM is a semiconductor with a conductivity of $1 \mu\text{Scm}^{-1}$ and main charge carriers are electrons. LTO is an ionic conductor its conductivity is $0.142 \mu\text{Scm}^{-1}$. In a SSFB, the lithium diffusion is very high and corresponds to conductivities up to 10mScm^{-1} . The use of EIS has been crucial to determine, from the magnitude of the associated capacitance, the main impedance contribution that limits the electrochemical performance of SSFB. We have assembled various half cells and full cells containing suspensions with different compositions. Results have shown that both the capacitive and resistive components of the contact resistance depend on the conductive additive e.g. Ketjenblack or Activated carbon. An electrical model has been developed that highlights the importance of the conductive additive on the semi solid suspensions. In order to optimize and improve the performance of SSFB, the resistance of the interphase region between the suspension and the current collector needs to be minimized considerably.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analysed. This technique is able to provide valuable information about the structural and elemental changes on the surfaces of the different materials used in the current collectors and in the electrolytes themselves. Pristine Cu (negative) and Ti (positive) current collectors and LTO and LMNC mixed with the conductive carbon, Ketjen Black 600D, have been analysed before and after the charge process, from 0 to 100% SOC. XPS analysis of fresh and charged samples of the current collectors and the electrolytes show significant differences, indicating evident changes in the structure and composition of the different surfaces. The changes in the surface of the different materials can be ascribed to the existence of secondary reactions and to the formation of several functional groups that may affect the performance of the system along time and the battery rate performance.

The main conclusions from the study of the interface current collector/slurry were:

- An (unusual) mechanical history dependence was found for KB suspensions, and connected to a plausible microscopic explanation via integrated analysis of both viscosity and conductivity. The yield stress and conductance of the KB network (at rest) can be tuned via shear history.
- Hetero-aggregation between KB and LTO, and probably also between KB and LiNCM could be demonstrated (in spite of KB-KB aggregation in the background).
- A rheometer could be modified into a setup that measures rheology and electrical impedance of the same fluid, while also allowing the fluid itself to be (dis)charged in situ.
- Electrochemical cycling (2.5-4.5 V vs. Li/Li⁺ for lincm, 1.0-2.5 V for LTO) has a (much) stronger effect on the electron conductivity of the KB (dominated) network, as compared to the rheological changes. This applies especially to KB-LTO systems.

- Starting from a computer simulation of a regular arrangement of rods, the particles assembled into a percolating network with no obvious crystal structure. The parameters were chosen to give a percolating network at a volume fraction of 0.6%.
- The contact resistance between current collector and electrode slurry has been identified, by means of EIS, as the main factor limiting the electrochemical performance of the SSFB. Results point out that the conductive particles determine to a large extent this contact resistance. An optimization of SSFB performance
- The changes in the surface of the different components of the SSFB (current collectors, particles the electrode slurries), as detected by means of XPS analysis, evidence the formation of different functional groups upon charging

3.4 Modelling

The objectives of modelling activities in the frame of the project were:

1. To understand the physical phenomena occurring at the microscopic scale;
2. To understand the rheology involved In SSFB;
3. To implement macroscopic model described in the literature and adapt them to InFLUENCE battery concepts;
4. To provide design recommendations leading to optimal interface behavior.
5. To optimize the overall geometry of battery in order to give recommendation for an industrial size.

These objectives were achieved by performing numerical modelling at various scales and by comparing calculated results with experimental data.

At molecular level (Objective 1), diffusion coefficients, density, viscosity were calculated for various solvents, ionic species (Li⁺, Na⁺) and particle volume fractions. Detailed kinetic mechanism for four electrode systems (TiO₂, ZnO, LTO, NaNCM) were developed and validated with experimental kinetic measurements. In terms of rheology (Objective 2), the behaviour of suspensions of solid particles was studied using the Lattice-Boltzmann model for particle volume fraction of 0, 5, 10, 20 and 25 %. Further experimental values were obtained from UTWENTE and IREC regarding the non-Newtonian behaviour of slurries (shear thinning: decrease of viscosity with increasing shear rate) for various compositions. Results from these two partners were heavily used as input in modelling studies, considering power law expressions.

At macroscopic level, the modelling of electrochemical cells in non-flowing and flowing conditions (objective 3) was performed using the COMSOL Multiphysics[®] software. Those results were obtained by solving electrochemical, rheological and diffusional phenomena simultaneously. Two different approaches have been considered: coupling of rheology with TiO₂ and NaNMC electrochemistry (secondary current distribution) and coupling of rheology with NiMH electrochemistry and diffusion

within solid and liquid phases (tertiary current distribution). Modelling studies and calculations following the mid-term meeting focused on modelling with LTO and LiNMC slurries (narrowed system) at various scales: laboratory cell (mono-channel), laboratory stack (single and multi-channel configurations) and larger electrochemical systems.

Conclusions from the modelling work have been used extensively in cell design (Objective 4 and 5). Calculations indeed led to the following geometry for the experimental set-ups:

- Single channel (74 mm length x 4-8 mm width x 1 mm thickness) for the electrochemical cell, designed and built in the early stages of the project.
- Multi-channel (100 mm length x 4 mm width x 1 mm thickness) with parallel configuration for the slurries flow for the electrochemical stack designed and built in the last year of the project.

Additional thermal and energy balance calculations were performed with the electrochemical stack. These calculations lead to recommendation for industrial size SSFB :

- maintain a relatively high surface to volume ratio to evacuate the heat easily;
- Using low thickness material for the cell constructions (to limit overheating caused by heat transfer through low thermally conductive material).
- Use of standard pumps for slurries flow in industrial systems.

Main S/T results

Modelling and comparison of calculated results with experimental data allows to put forward mechanistic relations at microscopic and macroscopic scale. This understanding is a prerequisite before considering industrial developments of SSFBs.

At the molecular level, self-diffusion coefficient, density and viscosity were calculated with various carbonate mixtures. Diffusion coefficient were calculated in the liquid phase for both Li⁺ and Na⁺ ions. Solvation structure and rheological behavior were also calculated. Diffusion coefficient of ions (Li⁺/Na⁺) in the solvent are in the range $10^{-10} - 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ depending on electrolyte compositions. These results are in agreement with experimental data. Viscosity vs shear rate calculations (IC) is consistent with partners measurements (UNIVERSITEIT TWENTE). Regarding the kinetic of oxidation and reduction reactions, detailed kinetic mechanism were proposed for TiO₂, ZnO, NCM and LTO. Calculations with COMSOL Multiphysics demonstrated the absence of diffusion limitations, in both liquid and solid phases during experimental measurements. For TiO₂ and LTO, it was found that one electrochemical reaction involving the Ti⁴⁺/Ti³⁺ couple was sufficient to obtain acceptable agreement between modelling and experimental results. For NaNCM, we considered a mechanism based on four electrochemical reactions, involving the Co⁴⁺/Co³⁺, Ni⁴⁺/Ni³⁺, Ni³⁺/Ni²⁺ and Mn⁴⁺/Mn³⁺ couples. For ZnO, the mechanism is based on successive reactions involving Zn/Na₂Zn₅, Na₂Zn₅/NaZn₂, NaZn₂/Na₂Zn₃ and Na₂Zn₃/NaZn coupled. Major electrochemical laws were considered as kinetic rate for the oxidation/reduction reactions, including Butler-Volmer (BV), linearized BV, Tafel, Nernst-Monod and the most recent Marcus-Hush-Chudsey (MHC) and Marcus-Hush (MH) laws.

The modelling at macroscopic level (lab-cell scale) was performed using the COMSOL Multiphysics[®] software. Two approaches were considered.

In the first approach we considered the design of the cell manufactured by IREC (channels with 74 mm length, 2 mm width and 1.5 mm depth) to perform rheology calculations. Velocity profiles and pressure drop calculations (3D, steady state) were performed considering non-Newtonian behaviour for the slurry. Results indicated that pressure drops were relatively small even for relatively short residence time (2 500 Pa for a RT of 0.1 hour). Investment in a pump with high pressure outlet is not required for lab scale experiments (input for task 2.2).

For the modelling of a SSFB in non-flowing conditions (steady state), we considered anodic slurry containing 15% Vol Anatase TiO₂ particle and a cathodic slurry containing 15% Vol NaNCM particles. Kinetics slightly modified compared to deliverable 5.11 (impact of SOC on quasi-equilibrium potentials taken into account) have been used as input in COMSOL Multiphysics[®]. Calculation of power versus current curves are consistent with standard battery physics.

For the modelling of a SSFB in flowing conditions, we solved simultaneously the equations associated with the fluid flow and electrochemistry calculation. Various discharge current and residence time values were considered for the calculation (parametric sweep study). Results indicated that various strategies are to be considered for SSFB operation, depending on the desired output. High current or low residence time values will result in high electrode particles SOC evolution and low cell voltage. On the contrary, low current or high residence time values will result in low SOC evolution and high cell voltage. Main results obtained with this approach are presented in the following figure:

In the second approach, separate computational domains were considered for the macro and micro scale levels. Only the combined modelling of the multiscale occurrences is accurate to fully understand the interfaces, as aimed by our InFLUENCE project. The liquid phase with the electronically-conductive nanoparticles is roughly regarded as a continuum at macro scale level, with either a tertiary current distribution or concentrated solution theory to resolve ion transport in the electrolyte bulk. To understand the SSFB interface however, the sub-micron scale active material was considered in a separate computational domain to describe solid-state diffusion.

Extensive modelling work was performed prior to the design and construction of the electrochemical stack. Calculations and discussion with partners (UNIVERSITEIT TWENTE, KIT, IREC, VITO, 6TMIC) lead to the final design: electrochemical stack consisting in parallel channel with a 4 mm width, 1 mm thickness and 100 mm length. Channels were parallel disposed to minimize heterogeneity and cell clogging. The low thickness value was chosen to minimize overpotentials and ohmic losses. The stack design of the electrochemical stack built in early 2016 is heavily based on modelling results and numerous interactions with InFLUENCE partners. The design chosen consist in a stack comprising three cells; each cell contains 6 channels with a 1 mm width, 1 mm thickness and 100 mm length. The total number of channels is therefore 18 for both anodic and cathodic slurries. The cell was delivered to IREC facilities with an innovative system for pumping the slurries (use of syringes). Low flow rates can be achieved with this system (residence time of 1 hour). Experiments with high flowrate were unsuccessful: slurry sedimentation cause high overpotentials and progressive clogging of the electrochemical stack. Further experiments were realized with the stack with a lower residence time value (1 minute), using a

peristaltic pump. Cell voltages around 5 V (2.5 V per cell) were obtained for three of the four electrical segments of the stack. Modelling results are in the same order of magnitude as experimental results. Modelling results are also consistent with experimental data in terms of SOC evolution and pressure drop. Difference between experimental and modelling results might be caused by undesirable side reactions (copper dissolution) observed experimentally. Modelling confirmed the interest of low tickness channel (1 mm) to minimize current homogeneities within the channel. Thermal balance was performed to evaluate temperature evolution between the cell inlet and cell outlet. A moderate increase (4°C) was calculated in standard conditions. Four and two tanks configurations were compared from a practical point of view. Two tanks configuration appears much more preferable for several reasons. Modelling was also performed to design a large industrial electrochemical stack, with a power outout of 1 kW. A stack consisting in hundreds of parallel channels with an individual length of 1.5 m and a tickness of 1 mm is appropriate to achieve such performance. An overall energy balance, taking into account energy losses, energy consumption by pumps and energy consumption by stirrers (for slurry tank), showed than energy generation was significantly higher than energy consumption, especially if stirrer are used in intermittent mode.

The main conclusions from modelling work were the following:

- SSFB performance (with conditions studied experimentally) are not limited by diffusion limitations within active particles or within the slurry.
- Electrochemical cells and stack can be operated with current densities around 20 A.m⁻² (contact area between the current collector and the slurry) with reasonable overpo
- Multichannel and mono-channel configuration can be used for cell and stack design. The multi-channel configuration is appropriate to obtain similar velocity profils within all channels.
- The channel tickness used for anodic and cathodic slurries shall remain low in order to maximize average current densities and decrease ohmic drops and poser losses. Modellig work indicated that a 1 mm tickness value is appropriate to design SSFB cells and stacks.
- A long residence time value shall be used to achieve complete charge or discharge in a single pass. These residence time values are associated with low velocities, causing slurry sedimentation and channel clogging. A different strategy has therefore been applied for SSFB operation, with higher flow rate and lower SOC evolution between the channel inlet and outlet.
- As full charge/discharge in a single pass is hardly achievable, a two tank configuration is preferable compared to a four tanks strategy. An industrial electrochemical stack with a 1.5 m length, a 1.5 m width and consisting in 10 superimposed electrochemical cell could potentially provide a power output (during discharge) around 1 kW. Applications for home applications (house) with this stack could be considered.
- Temperature increase with an electrochemical stack remains reasonable with low residence time value (1 minute). The use of forced convection (instead of natural convection) and the addition of heat removal fins on an industrial electrochemical stack shall not be required.

- Performance in terms of energy density are similar for SSFB and redox-flow batteries.
 - Performance in terms of power density are lower with SSFB compared to redox flow battery.
 - Higher current values and power density could be reached by further optimizing the slurry composition.
 - SSFB can be easily used in intermittent flow mode, which is not the case for redox-flox batteries.
-

4 Potential impact of the project

Understanding reactions at the **SEI** (solid electrode-electrolyte interface) in rechargeable batteries is essential to developing strategies to **enhance cycle life** and **safety** of rechargeable batteries. Despite past research efforts, there is still limited understanding by what means different components are formed at the SEI and how they influence SEI layer properties and behavior. The RTD activities carried out in the frame of the INFLUENCE project led to a better understanding of interfaces in Li-ion and Na-ion batteries, particularly the **formation** of the **(artificial) SEI layer**. In addition to the study of this aspect, of paramount importance for all rechargeable batteries, the investigation of interfaces in fluid electrodes led to a more thorough understanding of interface aspects that could not be obtained from the study of conventional batteries.

In conventional Li-ion battery anodes (graphite based) a good SEI is electronically insulating and ionically conductive to electrically passivate the surface and avoid further decomposition, which enables safe operation beyond the stability window of the electrolyte. However, in **fluid electrodes**, the active particles are in continuous motion and the electronic conductive pathways are rather dynamic. The contacts for electron transfer between current collector and particles are severed and re-established continuously, which allows the SEI to cover the entire current collector. Thus, the **SEI** in **SSFBS** is mostly located between the current collector and the fluid electrode. Once the SEI is formed in SSFBs, the electrons must cross this electrically **insulating barrier** on their way from the current collector to the active material and vice versa. The electrically insulating character of the SEI turns from a beneficial feature in classic LIBs to a **detrimental** one in SSFBs. A non-electrically insulating SEI does not prevent the electrolyte decomposition and the potentials beyond the SEI formation are not accessible. Either way, operating outside the **stability window** of the electrolyte solutions does not seem possible in SSFBs.

The project led to specific insights in the **rheology of electrochemically active slurries**, in the particle interactions (aggregation, network formation, segregation) and in the behaviour of their individual components and of the. To ensure electrical conductivity within the electrode slurry, conductive particles were added to the dispersions in the electrolyte medium. The percolation behaviour was studied under flow conditions. **Rheological** and **electrical** properties were measured in conjunction, also in combination with (dis)charging currents. This **combination** of techniques and **scope** of application is **novel**. The rheological and conductive properties of the fluid electrodes at a given composition were found to depend on the mechanical formulation. The contact resistance between current collector and electrode slurry has been identified as the main factor limiting the electrochemical performance of the SSFB. Results point out that the conductive particles determine to a large extent this contact resistance.

The **enhancement** of the energy density in **SSFBS requires** either thus the search and development of **novel active materials** operating at 1.2–0.8 V vs. Li/Li⁺ or the **replacement** of carbonate-based **electrolyte solution** by others which are more stable at very cathodic potentials such as some **ionic liquids**. Until now, materials operating at 1.2–0.8 V vs. Li/Li⁺ were of little interest for the battery community due to their lower energy density. Now, materials such as Sb, ZnSb, Bi, black phosphorous or metal phosphides (e.g. NiP₂), operating above 0.5 V vs. Li/Li⁺ may deserve the attention of the battery community for the next generation of SSFBs.

Sodium-ion batteries are attracting increasing attention. Nowadays, they are considered as a future alternative to Li-ion batteries for **large scale energy storage** applications, because they possess a **cost advantage** with respect to Li-ion batteries due to the lower costs of sodium based raw materials and the replacement of the copper anode current collector with cheaper aluminum. Energy densities up to 200 Wh kg⁻¹ may be achievable. Na-ion battery technology is still considered to be in its infancy, and new active materials are developed rapidly. The set-up and working principle of both battery technologies are similar, which facilitates the transfer of Na-ion batteries into application. A part of the RTD activities within INFLUENCE focussed on Na-ion battery technology. **Novel NaNMC layered Na-based oxides** were synthesised, optimisation and characterised, revealing very promising behaviour as positive electrode for Na-ion batteries. NaNMC materials were also tested in different battery systems, both conventional solid Na-ion batteries and SSFBs. These activities resulted in an **advancement** of the knowledge on **Na-ion batteries** and their state of development.

4.1 Socio-economic impact and wider societal impact of the project

In a wider perspective the INFLUENCE project makes a contribution to the implementation of the SET-Plan. The availability of storage technologies suitable for integration with RES is key to ensure an increase of the share of RES in the energy mix. There is a need for a next-generation storage systems, which should allow absorbing energy when the generated power exceeds the need and releasing energy when the demand is higher, stabilizing then the intermittent renewable energy. This constitutes a key to large-scale deployment of renewable energy and absorption of distributed power in the grids, crucial in order to reach 2020 and 2050 energy and climate targets. SSFB, the battery technology studied within INFLUENCE is an energy storage technology highly suited for integration with RES.

For grid-scale storage based on conventional Li-ion batteries, thousands of cells are assembled since the capacity of Li-ion cells is not very high. This has a negative impact on costs (due to the assembly of and the monitoring electronics for each cell), the safety (every individual cell can fail) and reliability (if one cell ages in a string whole this string cannot operate anymore). Conversely, these systems deliver power performances better than actually needed. In a conventional solid Li-ion or Na-ion battery, power and energy are intrinsically linked since the active materials are inside the battery. RFB technology offer a solution to the limitations of Li-ion batteries. In RFB batteries the active materials are stored in containers and pumped through cell stacks that deliver the power. A remarkable characteristic of RFBs (including SSFBs) is the fact that power and energy are decoupled. This is not only important for safety, but also for reliability: a vast amount of energy to be stored does not imply the need for huge amount of cells (high statistical opportunity of failure). Since the active materials are stored in tanks, more energy can be stored just by increasing the amount of active materials. The performance of conventional RFBs does not allow grid-scale distribution and storage because the individual cells do not deliver enough power and the energy density is too low. Both aspects would lead to a gigantic storage size. SSFB technology, the system in which INFLUENCE studies focused, combines RFB technology with Li (Na)-ion active materials. In consequence, with SSFB technology power and energy are decoupled while power performance derives from Li-ion active materials and is thus notably improved in comparison with conventional RFBs.

RFBs and SSFBs have an analogous way of operation and are suitable for similar applications. The main difference is that in SSFBs the active materials are largely the same as used in Li-ion and Na-ion batteries, offering higher energy density than regular RFBs, and therefore occupying smaller volumes to store the same amount of energy. Consequently, SSFB seems very suitable for applications urbanized areas. SSFB can be deployed for integration of variable distributed generation, commercial and industrial energy/power management for which power requirements are in the range of 100-1000 kW and duration time of 2-10 hours. It must be clear however that the strength of SSFBs is on high-energy applications instead of high-power. Still, the power is much higher compared to conventional RFBs.

4.1.1 Contribution to the international standardization framework

Standards are under development for large Li-ion battery systems and for the use of energy storage in a broader sense in electricity grids. Safety and reliability are important aspects that have to be covered by standards. Fundamental understanding of battery behaviour is mandatory for this. VITO is member of IEC SC21A WG5 that prepares a standard for storage based on large Li-ion cells. The knowledge developed in the InFluENCE project will be brought to the standardization committee.

4.1.2 Contribution to rational and sustainable use of resources

An impact on rational use of resources is the application of Na-ion materials since sodium is much more abundantly available than lithium. This said, lithium or sodium only contributes a small fraction of the total material usage in the active materials. Therefore, recycling remains important.

Recycling is crucial for the market penetration of energy storage systems. The EU battery directive (2006/66/EC) implies that the only option for (H)EV or stationary batteries is second life or recycling. Removing the active materials is easier in a flow battery set-up than in a classic battery configuration.

4.1.3 Competitiveness of European industry. Impact for industrial partners of the project.

Storage is important for the European electricity grid and electrochemically based storage has a clear position in it, as explained in the section on smart grids above. Most of the batteries are made nowadays in Asia (Japan, China, Korea). Fundamental understanding of battery behaviour leads to increasing the competitiveness of the European industry. Two aspects of the project reinforce this:

- Solvionic, an SME active in the field of specialised materials are already valorizing some of the developments from the project.
- The work on computational modelling was coordinated by 6TMIC, a SME, which gained a leading position in the field.
- The knowledge gained in safety aspects can be used in standardisation activities.
- The semi-solid flow battery is both a better concept for storing renewable energy in the European electricity grids than Li-ion batteries or redox flow batteries alone.

In summary, the outcomes of this project bring a contribution to development of new energy conversion technologies and their commercial deployment, paving the way towards a low-carbon economy.

4.2 Dissemination activities and exploitation of the results

4.2.1 Dissemination

Non IP-sensitive project results were disseminated through various channels, the most frequent being SCI publications and communications in scientific conferences. A total of 13 SCI publications related to the project have been realized; additionally three publications dealing the latest developments on the project are under review/preparation and will be published in the coming months. Out of these 13 publications, 10 are open access. Project results were also communicated to scientific conferences (28 communications). A detailed list of SCI publications and all other dissemination activities are given in Template A1 and Template A2, respectively.

A project website was designed and launched beginning of December 2013. While the login area of the website was intended for internal project purposes, the public part of the website is intended as dissemination tool for the wider public. Non confidential documents are made accessible to the general public under the menu “downloads”, e.g. a general presentation about the project or links to SCI papers published open access.

4.2.1.1 Organisation of workshops

KIT organized in November 2014 a topical workshop on active materials in conventional lithium-ion and sodium-ion batteries in the Helmholtz Institute in Ulm. This workshop makes part of the dissemination activities planned in the frame of the EU-FP7 project Influence to favour dissemination of knowledge within and outside project.. Two out of the six presentations will be delivered by speakers external to the project, from internationally renowned research groups in the field (namely Prof. Roberto Marassi and Prof Vito di Noto). The focus of this first workshop was on the interfaces of active materials in conventional metal-ion batteries (e.g.: Li, Na, Mg). Some recent results originating from the project were presented, specifically concerning Na based active materials. One presentation on conventional redox flow batteries was included as well, as their state of the art is most relevant for the developments in the frame of the Influence project.

A 2 day course on electrochemical engineering and modelling (with special regards to batteries) was organized by VITO. The course took place on 27 and 28 August 2015 in the VITO satellite offices in Antwerp (Belgium). Four out of the six lectures were delivered by speakers external to the project. The external speakers were Prof. Digby Macdonald (UC Berkeley, USA), Prof . Mirna Urquidi (Penn State University, USA), Prof. Theo Tzedakis (Univ Toulouse III, France) and Prof. Philippe Barboux (Chimie Paristech, France). The lectures by each of the external speakers consisted of 3 blocks of 45 min (2h30 minutes lecture per speaker with short breaks included). The lectures by the 2 speakers from the Influence consortium, Dr. Xochitl Domínguez (VITO, Belgium) and Dr. Remy Lacroix (6TMIC Ingenieries, France), consisted of 2 blocks of 45 min (1h30 minutes total per speaker). The topics covered in the lectures offered interesting insights for junior R&D professionals working in the field of battery research.

In order to facilitate the interaction between the speakers and the attendees, the size of the group was kept small (. No participation fee was requested (participants must however to arrange their travel and accommodation expenses). Further details can be found in D6.32.

IREC organized a topical workshop on rheology and system design of flow batteries, which makes part of the dissemination activities planned in the frame of the EU-FP7 project Influence. The duration of the workshop was half a day. Seven lectures of ca. 25 minutes each were delivered by speakers specialised in areas relevant to the topic. The workshop counted 47 attendees, out of which 34 external to the Influence Consortium. The focus of this last workshop was on flow batteries and analogous devices. Some recent results originating from the project were presented, specifically concerning rheological investigations on fluid electrodes. One presentation on battery standardisation was included as well, as cross-cutting issue in battery research. The external speakers were Dr. Jens Burfeind (Fraunhofer UMSICHT, Germany), Dr. Carlos Ponce de Leon (University of Southampton, United Kingdom), Dr. Belabbes Merzougui (Qatar Energy & Environment Research Institute, Qatar) and Juhan Lee (INM - Leibniz Institute for New Materials, Germany). Further details can be found in D6.33.

4.2.1.2 Target Groups

The INFLUENCE project aimed to engage a number of stakeholders at different dissemination levels. The target audience could be classified in groups as follows:

- Scientific Community was widely addressed via the usual means: SCI publications, communications in scientific conferences, workshops organised in the frame of the project.
- Industry: manufacturers of components and whole batteries; enterprises active in innovative energy technologies, as they also attend conferences dedicated to battery technology.
- Wider Public has access to information about the project and its progress via the public website www.fp7-influence.eu.

For detailed information about dissemination activities see document in attachment "Influence 608621 PUDF (dissemination part) v2.0".

4.3 Exploitation

An FTO analysis was made at the beginning of the project regarding the existing pending patent applications on SSFB technology, in the name of Massachusetts Institute of technology (MIT) and/or 24M Technologies Inc, or others. The existing patents did not seem critical for the areas of commercial interest of the industrial partners.

Some of the project foreground is being exploited, directly or indirectly, by SME partners (Solvionic and 6TMIC). Since the start of the project, one of the industrial partners - Solvionic- devoted their activities in the project to the development of ionic liquids for application in batteries. The work being carried out in INFLUENCE gave Solvionic the opportunity to select, improve and understand their materials for Li-ion and Na-ion (semisolid flow) batteries. Solvionic is a young player for electrolyte systems, with a material that is nowadays not used in commercial batteries: ionic liquids. Their formulations for the slurries are key to the stability of the suspensions. For them it may open a new market, since commercial Li-ion batteries use nowadays no ionic liquids. The work program of INFLUENCE contributed to the

development of ILs based electrolytes for application in electrochemical energy storage (EES) systems and help Solvionic and the European industry to integrate the supply chain of electrolytes for EES systems including new semi solid flow batteries, but also Li-ion or Na-ion battery. 6TMIC is an engineering and technology transfer company active in electrochemical engineering and numerical modelling. They have a strong background in optimizing the design of electrochemical systems to improve their performance. The exploitation goal of 6TMIC is to offer engineering services. The main path for exploitation of project foreground by RTO/university partners is the execution of new research projects, where the knowledge and experience gained in INFLUENCE can be applied and advanced further. Multiphysics modelling of battery processes and systems is the main ground of exploitation for VITO. In the case of KIT, the focus of exploitation is on optimised materials and formulations for Na-ion batteries. Universiteit Twente focus their exploitation actions on novel method for electrochemical charging of slurries inside a rheo-impedance setup. For IREC the main ground for exploitation is on formulation and operation of SSFBs. Also, in some cases the knowledge is implemented in university courses or lectures in master programmes.

An overview of exploitable project foreground is given in template B2 (confidential information).

5 Contacts

Website of the project: www.fp7-influence.eu

Project logo:



5.1 Project Coordinator:

VLAAMSE INSTELLING VOOR TECHNOLOGISCH ONDERZOEK N.V. (VITO)

Boeretang 200

2400 MOL

Belgium

Contact: Dr. Yolanda Alvarez-Gallego

Tel. +32 (0) 14335612

E-mail: yolanda.alvarezgallego@vito.be; fp7-influence@vito.be

5.2 Project participants:

KARLSRUHE INSTITUTE OF TECHNOLOGY (KIT)

Helmholtz Institut Ulm (HIU)

Helmholtzstraße 11

89081 Ulm

Germany

Contact: Prof. Dr. Stefano Passerini

Tel. +49 (731) 50 34101

E-mail: stefano.passerini@kit.edu

UNIVERSITEIT TWENTE

Dept. Science and Technology

PO Box 217

7500 AE Enschede

The Netherlands

Contact: Dr. Michel H.G. Duits

Tel. + 31 53 4893097

E-mail: m.h.g.duits@utwente.nl

FUNDACIO INSTITUT DE RECERCA EN ENERGIA DE CATALUNYA (IREC)

Jardins de les Dones de Negre 1, 2^a pl.
08930 Sant Adrià de Besòs (Barcelona)
Spain
Contact: Prof. Dr. Joan Ramón Morante
Tel. + 34 933 562 615
E-mail: jrmorante@irec.cat

ECKART GMBH

Guntersthal 4
91235 , Hartenstein
Germany
Contact: Stephan Roth
E-mail: Stephan.Roth@altana.com

SOLVIONIC

Site Bioparc Sanofi
195, route d'Espagne -BP1169
31036 Toulouse cedex 1
France
Contact: Sebastien Fantini, Ph. D.
Tel. +33(0)5 34 63 35 35
E-mail: contact@solvionic.com)

6T-MIC INGENIERIES (6TMIC)

51 rue Ampère - Bat Stratège A
31 670 Labège
France
Contact: Dr. Serge Da Silva
Tel. +33(0) 5 34 43 63 39
E-mail: contact@6t-mic.com

UNIVERSITY OF CAMBRIDGE (UCAM)

Trinity Lane The Old Schools
CB2 1TN Cambridge
United Kingdom
Contact: Prof. Dr. Daan Frenkel
Tel. +44(1223)336377
E-mail: df246@cam.ac.uk