

Assessment of the Li-air battery technology for automotive applications through the development of a multi-electrode solid-state prototype

Alexis Laforge, M. Toupin, A. Mokrini, M. Gauthier,
C. Bock, M. Ionescu, X.Z. Yuan, W. Qu and J.Y. Huot

June 21st 2016 – EVS29



National Research
Council Canada

Conseil national de
recherches Canada

Canada

About NRC

Canada's Research and Technology Organization (RTO)

- \$909.3M budget (2014-2015)
- 3,550 employees

Serves thousands of industrial and government clients annually



Booth #1515

▼ IRAP

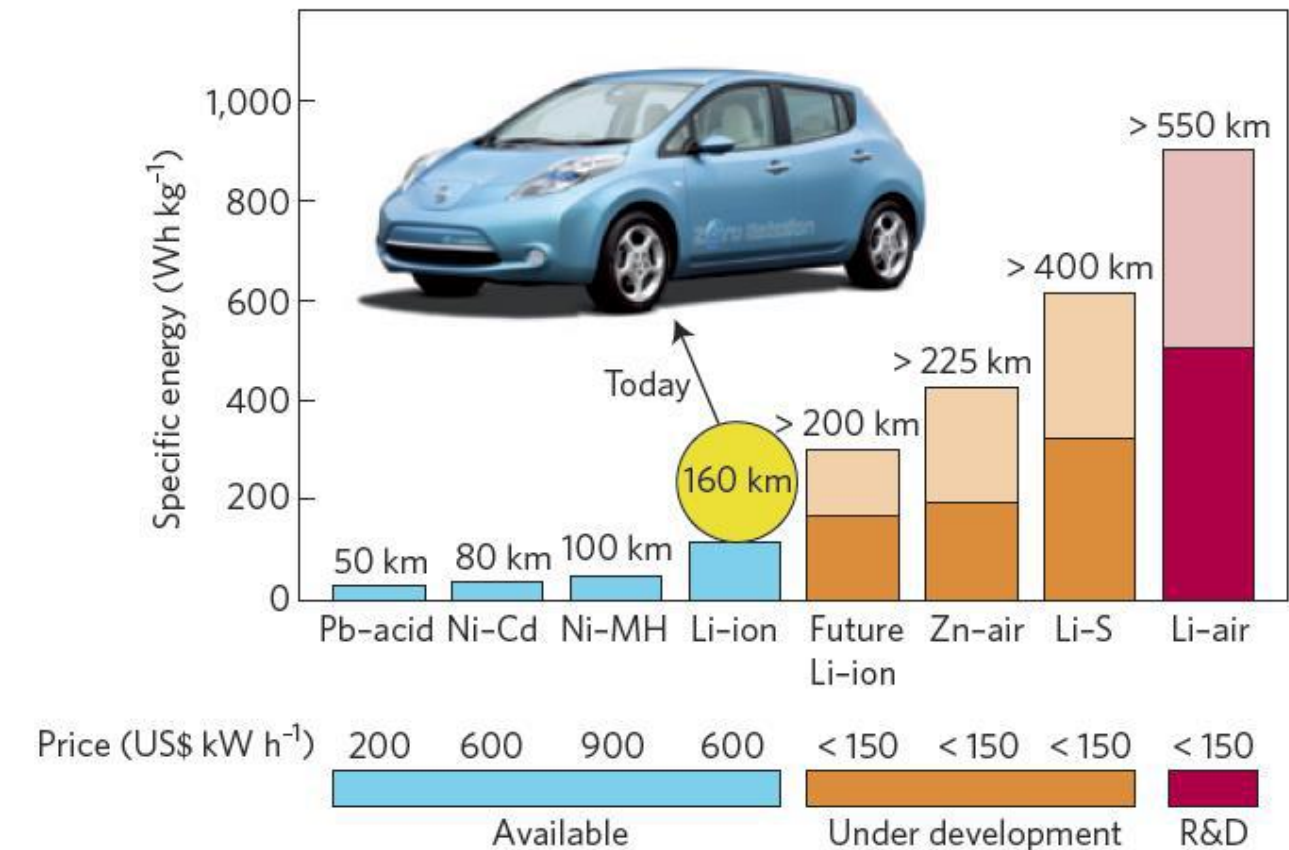
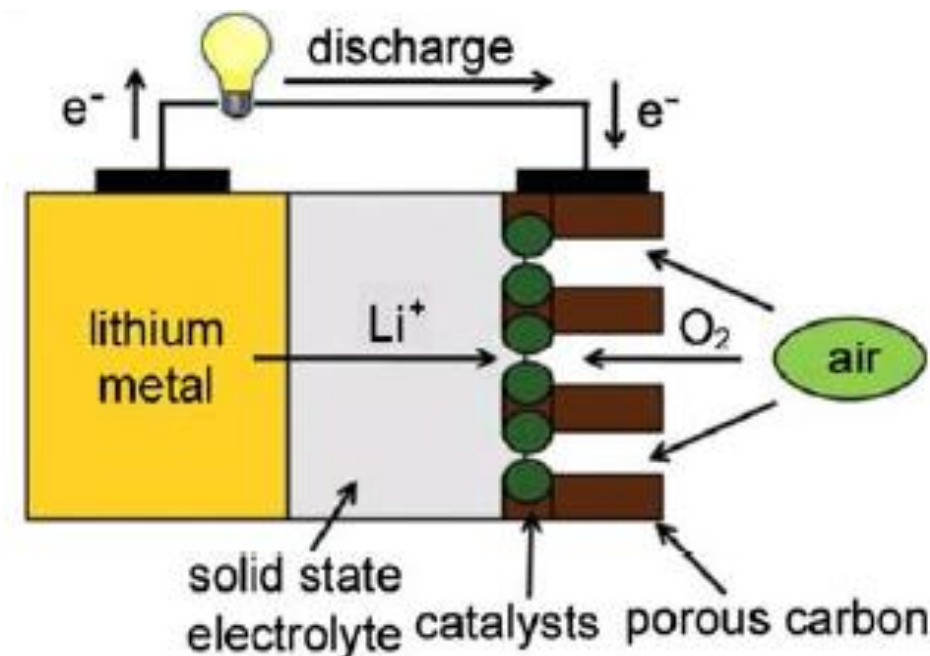
■ Research Facilities

NRC-CNRC

Li-air technology : the promises

The concept

By combining metallic lithium at the anode and oxygen from the air at the cathode, huge energy density can be achieved (theoretically 3500 Wh/kg Li_2O_2)



The promises

Reaching an energy density of 1000 Wh/kg (5 times current Li-ion technologies) would allow EVs to reach over 500 km in a single charge.

Li-air technology : the challenges

Anode

- Lithium dendrites prevention (safety)
- Protection against oxygen and air contaminants

Electrolyte

- Physical stability (negligible evaporation)
- Chemical/electrochemical stability (lithium, Li_2O_2 , $\text{O}_2^{\cdot-}$, ...)

Cathode

- Chemical/electrochemical stability (Li_2O_2 , $\text{O}_2^{\cdot-}$, ...)
- Catalytic efficiency (overpotentials, coulombic efficiency)
- Electrochemical kinetics (power density)
- Tolerance to gas impurities (H_2O , CO_2 , ...)

Scale-up

- Large-scale battery design, gas flow, ...
- Upscaling of components and assembly methods

NRC Li-air project : objectives

MAIN OBJECTIVE : assess the Li-air technology for automotive applications

➡ **Develop and evaluate a realistic pilot-scale Li-air battery prototype**

Electrolyte (+ anode)

- Develop a protective and dendrite-blocking electrolyte
- Compatibilize the solid polymer electrolyte with the porous cathode

Cathode

- Develop thin and ultra-porous nickel foams
- Screen-test a series of potential catalysts and supports
- Optimize the deposition method and active material loading

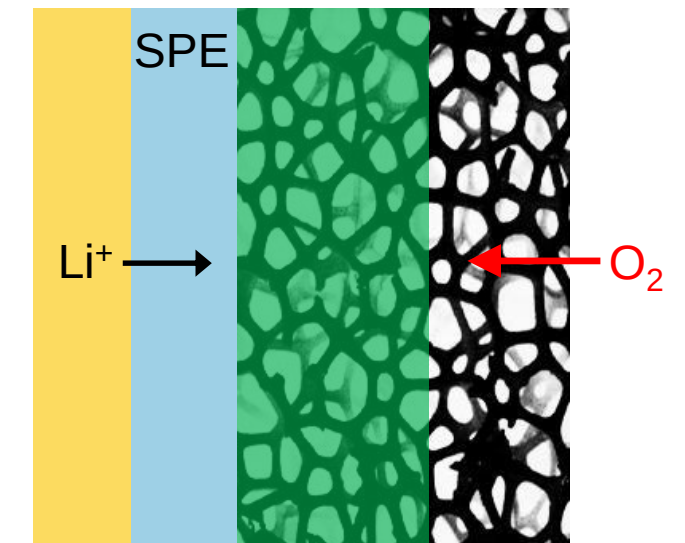
Scale-up

- Design a scalable multi-electrode prototype
- Upscale the components and assembly methods

R&D on materials and components

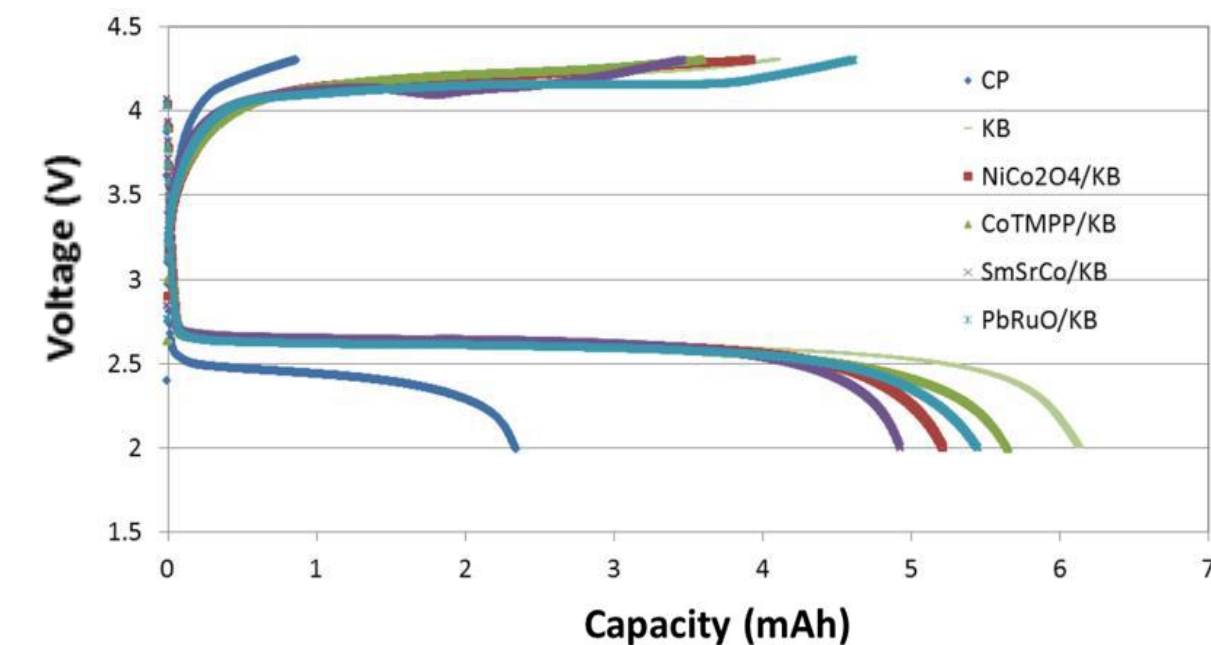
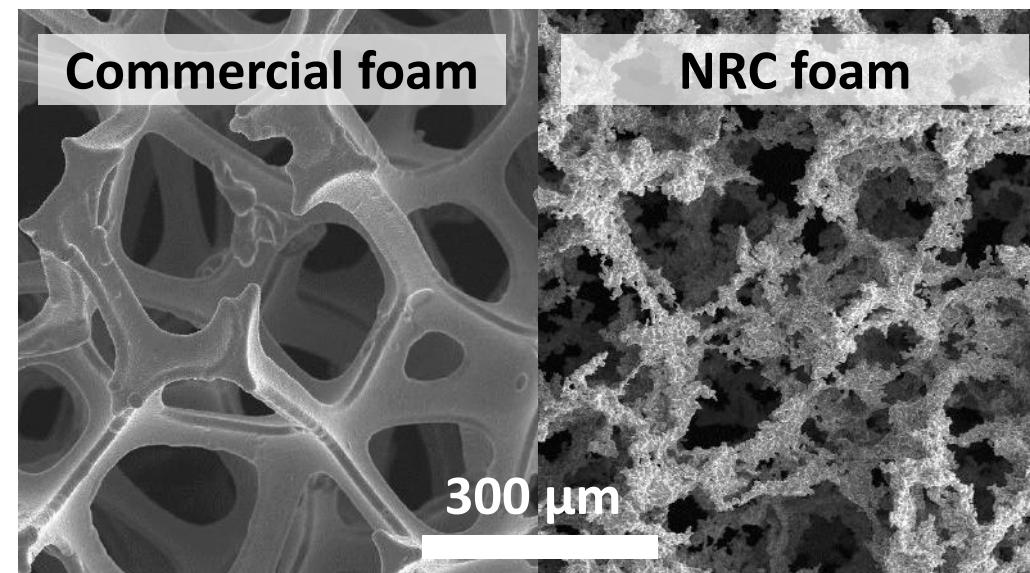
Solid-state polymer electrolyte

- ✓ Processed using melt-extrusion in an anhydrous room (-60 °C dew point)
- ✓ High ionic conductivity (above 60 °C)
- ✓ High O₂ permeability
- ✓ Improved resistance to dendrite growth



Cathode

- ✓ Special nickel foams developed
 - High porosity (> 90 %)
 - Smaller pore size (< 200 μm)
 - High surface area (→ better electronic transfert)
 - 30 % weight decrease vs. commercial foams
 - Scale-up difficult (still in progress)
- ✓ Numerous catalysts evaluated
- ✓ Several catalytic supports tested

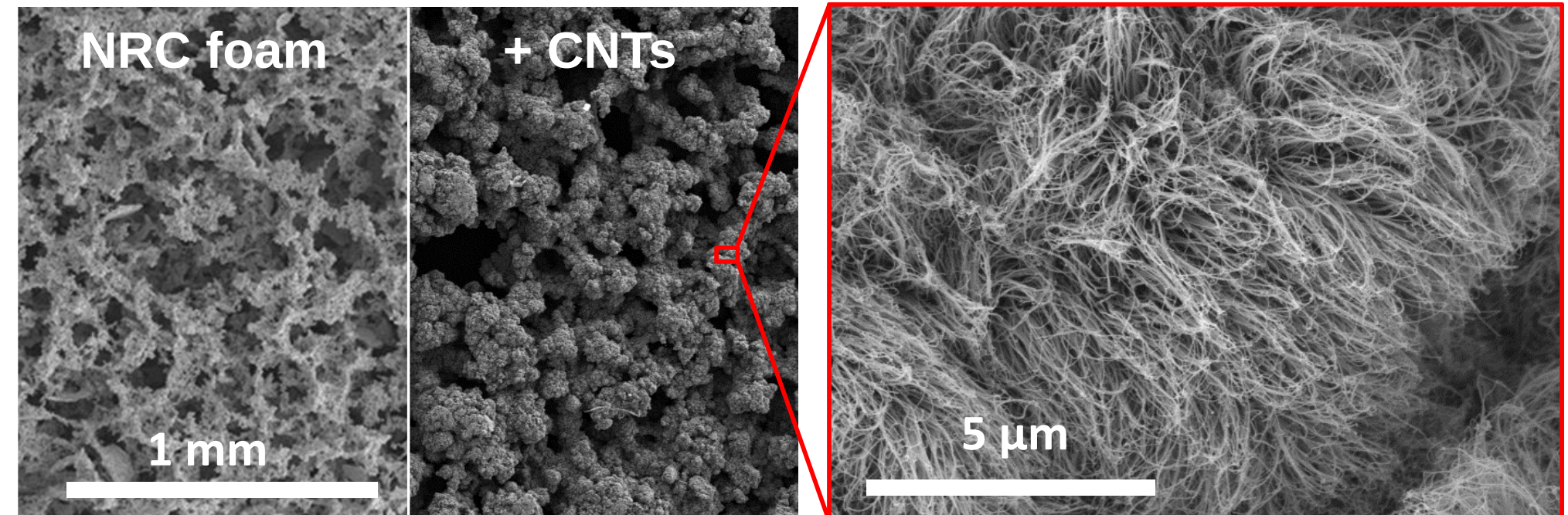


R&D on component integration methods

Active materials 3D deposition

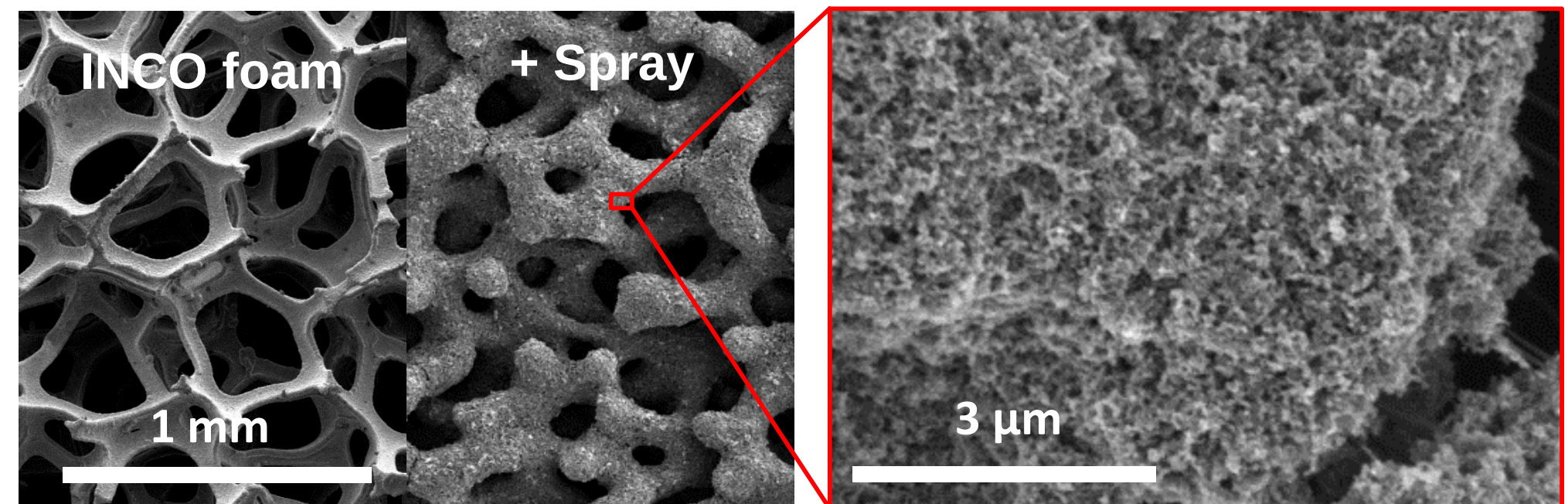
✓ Direct deposition of carbon nanotubes (CVD)

- High loading (up to 10 mg/cm²)
- No binder
- High capacity (5000 mAh/g)
- Scale-up difficult (though not unrealistic)



✓ Spray-coating of active formulations

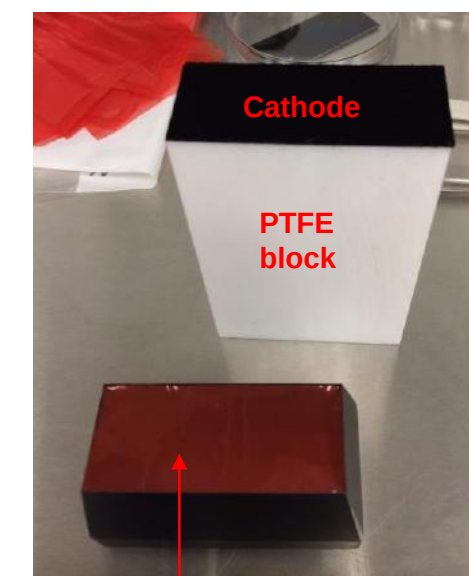
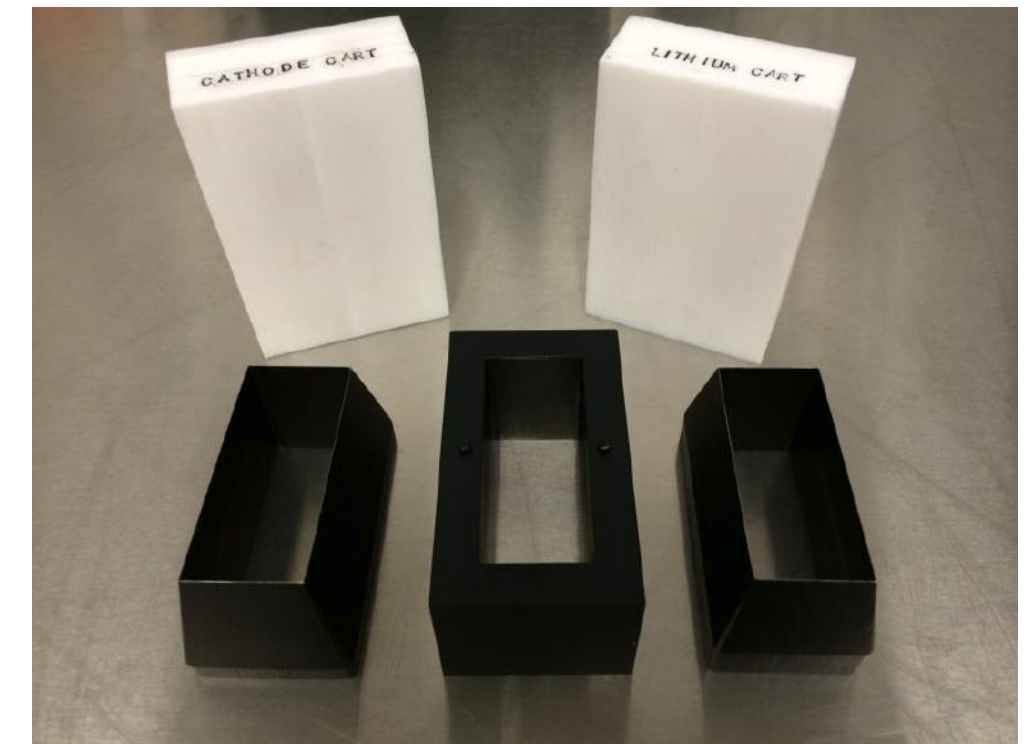
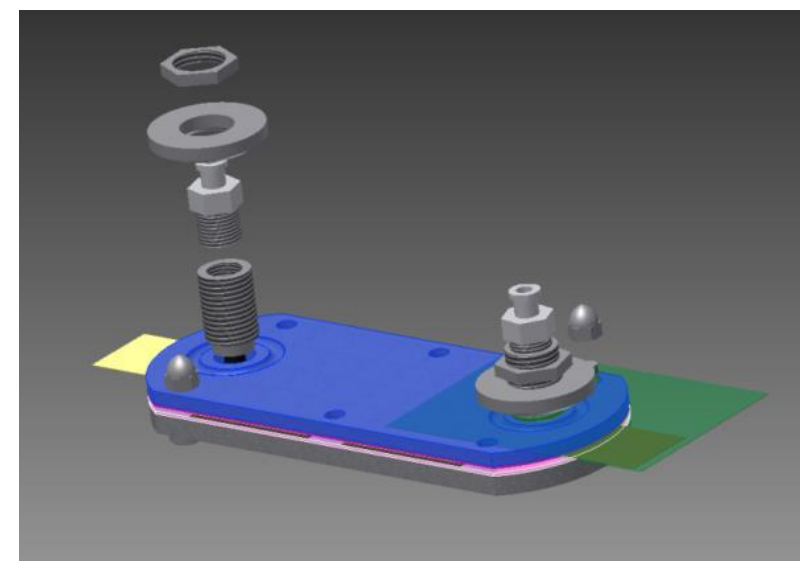
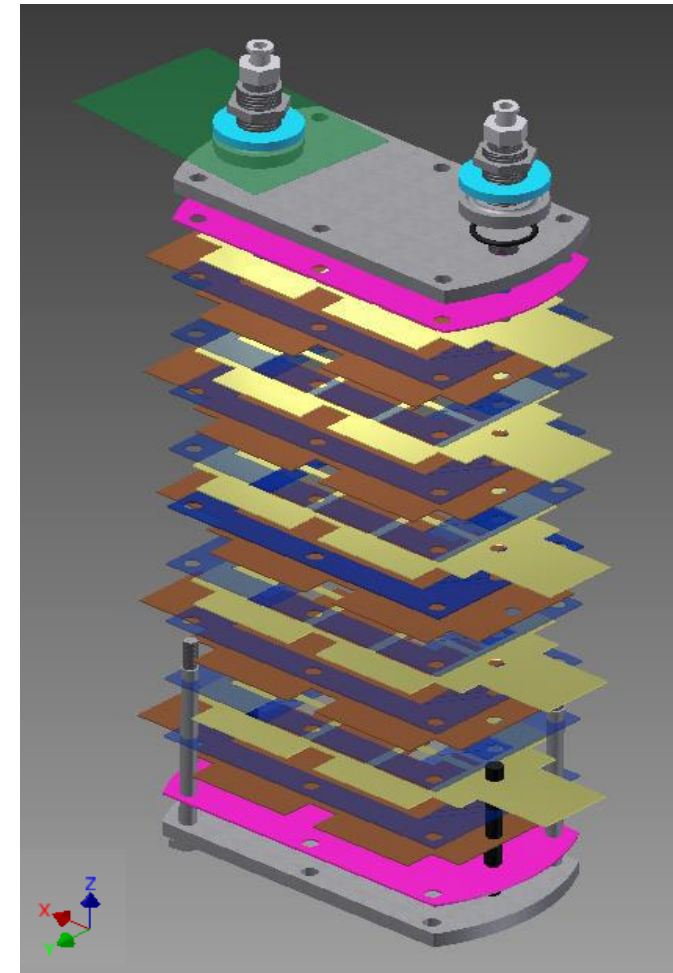
- High loading (up to 5 mg/cm²)
- Flexible (formulations can integrate catalysts)
- High capacity (4000 mAh/g)
- Easy scale-up (scanning spray deposition)



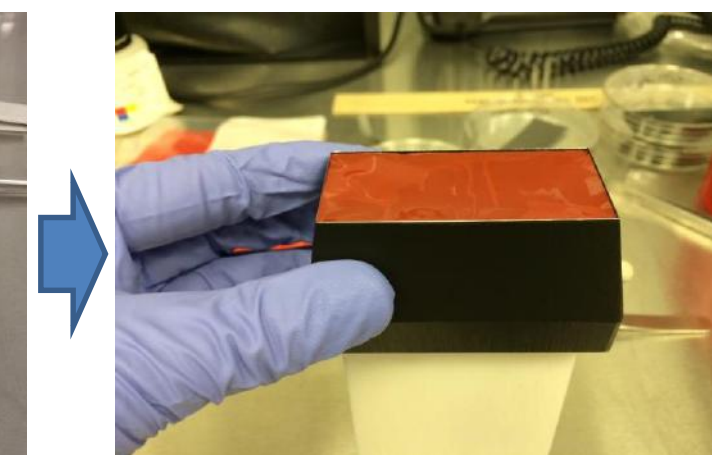
Prototype design and assembly methods

Scalable multi-electrode design

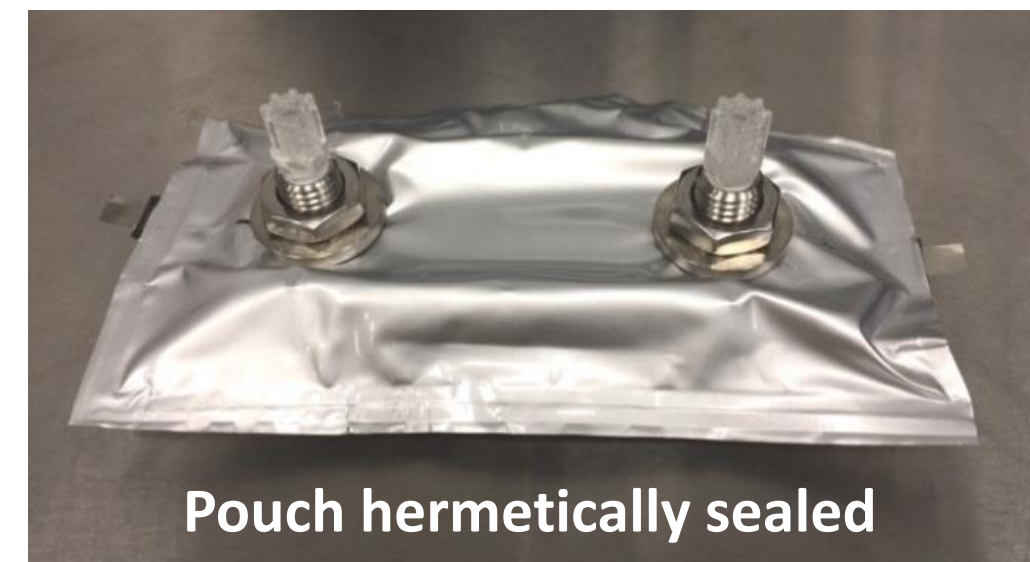
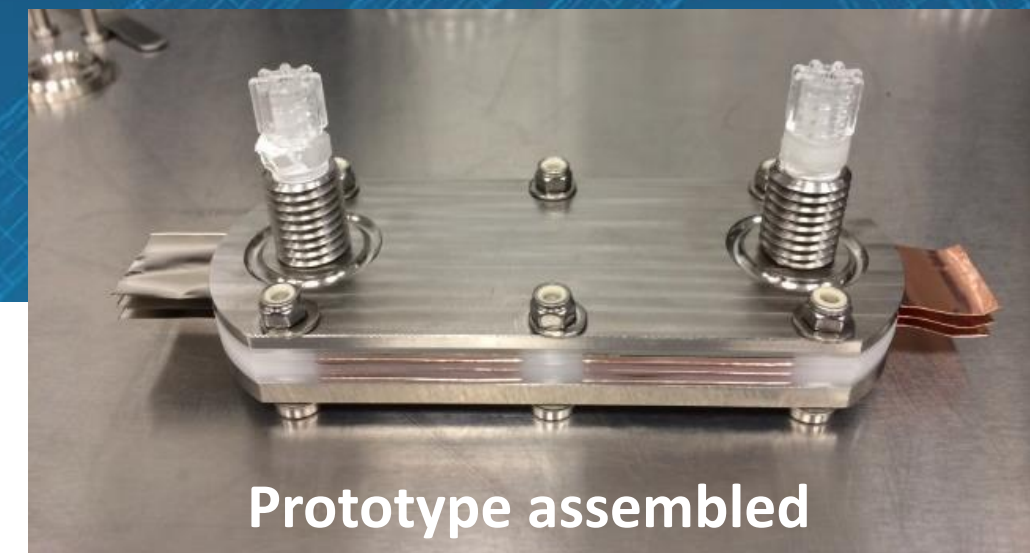
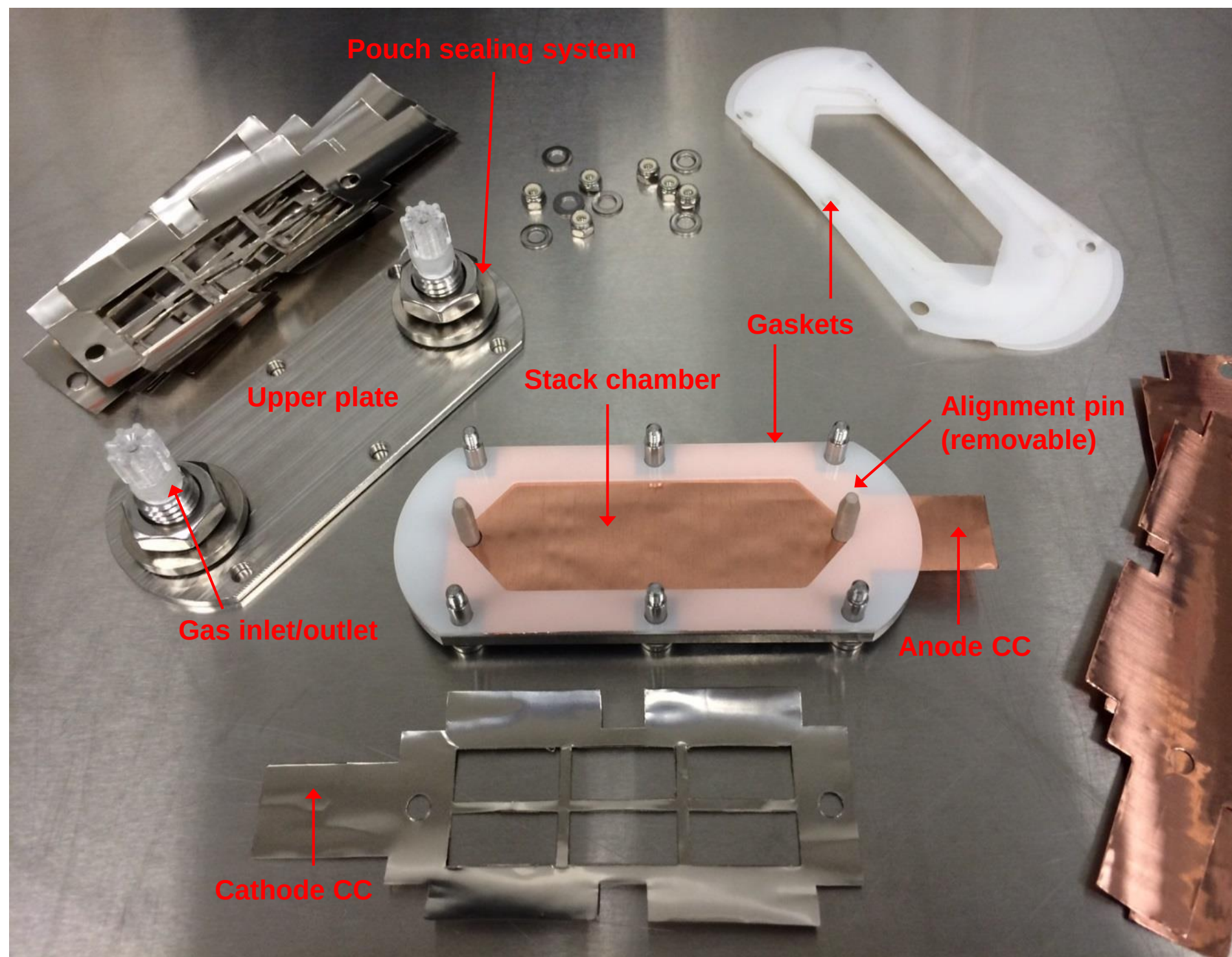
- **Design of prototype**
 - ✓ Pilot-scale : 100 cm² of active area (x 80 vs. coin cell)
 - ✓ Scalable : easy increase of active area
 - ✓ Realistic : multi-electrode stacking
⇒ Gas flow distribution
- **Upscaling of components**
 - ✓ Electrode size : 20 cm² (2.95 x 6.75)
 - ✓ Automated scanning spray deposition
 - ✓ Extrusion of polymer components
- **Design of specific tools**
 - ✓ Components for precise alignments
- **Assembly methods**
 - ✓ Manufacturing quality and reproducibility



Integration layer with PTFE backing layer punched to cathode size (backing layer on top)

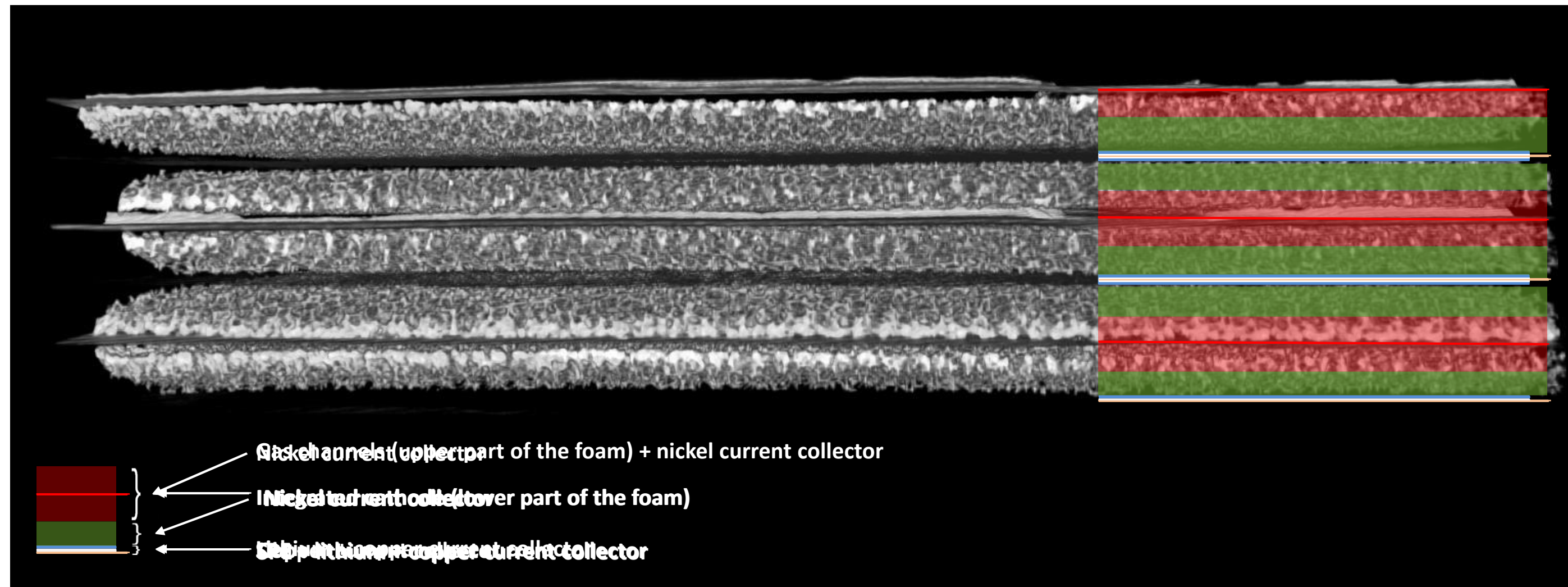


Prototype assembly



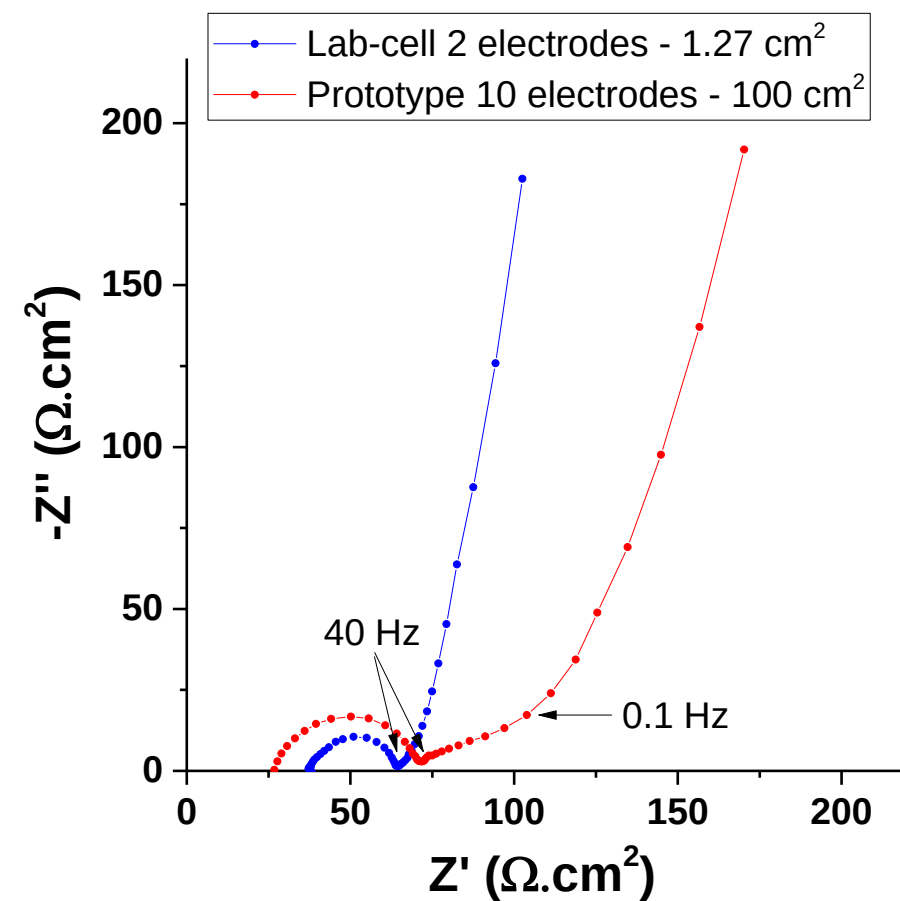
Prototype assembly characterization

Characterization using X-ray microtomography (micro-CT)

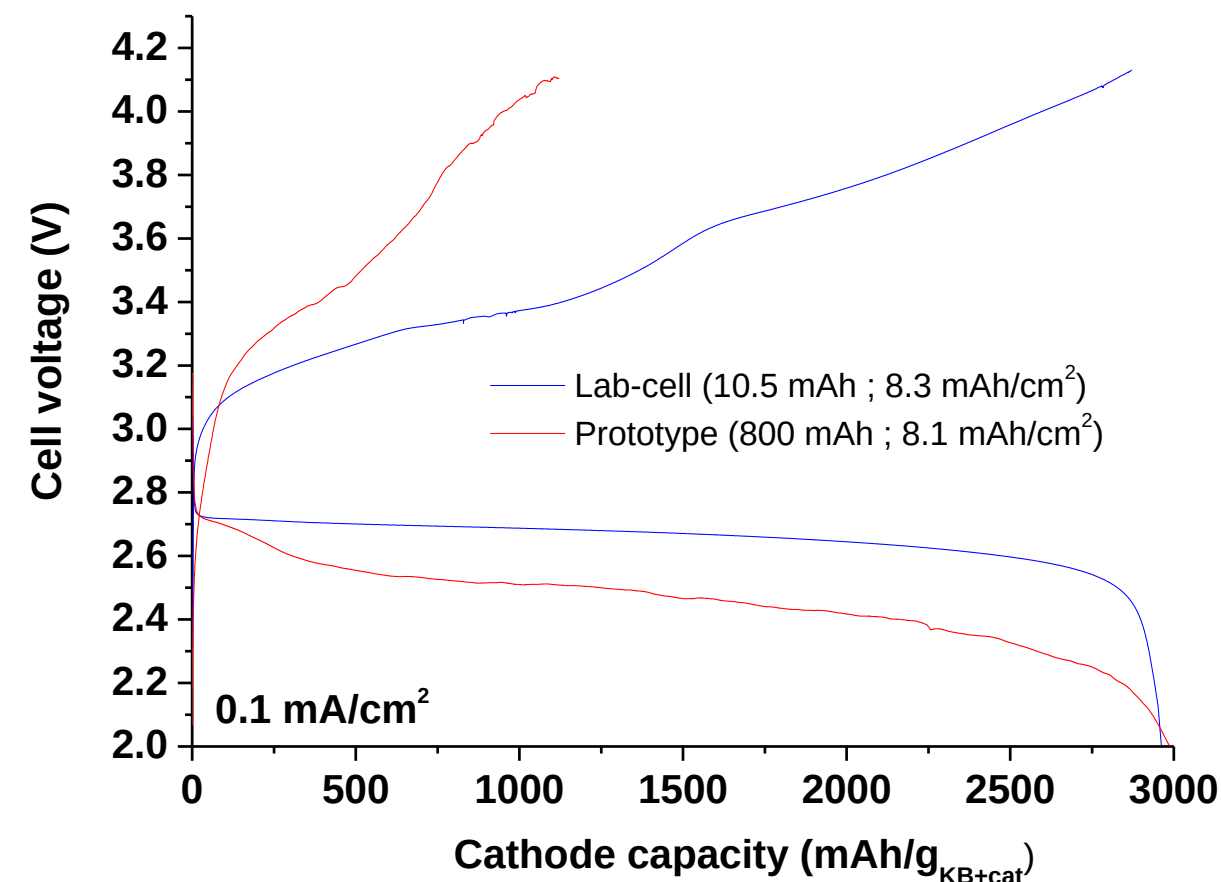


Electrochemical performances

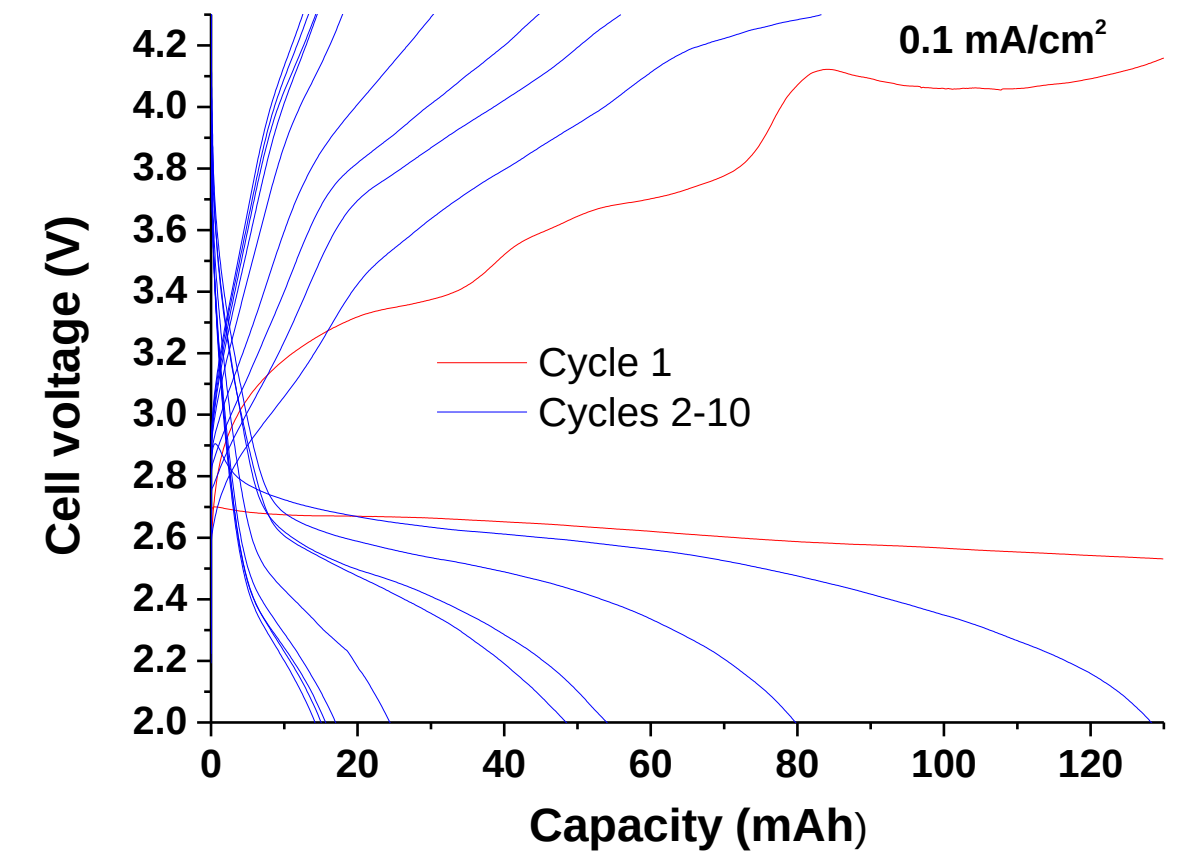
Impedance spectroscopy



Discharge capacity



Cycle stability



- Impedance and capacity performances reproduced quite well those of lab-cells but also showed an issue of O_2 diffusion (Warburg behaviour at medium frequencies, 200 mV lower discharge voltage)
- No rechargeability at 100% DOD
- Poor cycle stability at 15% DOD shallow cycling (chemical unstability of Li_2O_2)

Electrochemical performances

Energy performance assessment

- Prototype capacity : 800 mAh
- 2.5 V average discharge voltage → energy : 2 Wh

LEVEL	GRAVIMETRIC ENERGY DENSITY	Energy density Charged (no $\text{Li}_2\text{O}_2/\text{O}_2$)	Energy density Discharged (+ $\text{Li}_2\text{O}_2/\text{O}_2$)
➔	Cathode active materials (260 mg + 2.58 g Li_2O_2)	7700 Wh/kg	700 Wh/kg
➔	Stack (8 g + 1.79 g O_2)	250 Wh/kg	204 Wh/kg
➔	Stack (if optimized: + NRC foams & 2.7 V discharge)	325 Wh/kg	250 Wh/kg

	VOLUMETRIC ENERGY DENSITY	Energy density
➔	Stack (11.2 cm^3)	180 Wh/L

Summary

In order to assess the readiness of the Li-air technology, a large-scale multi-electrode prototype was developed and tested.

- Ultraporous thin nickel foams sheets were developed, leading to a 30% reduction in weight compared to commercially available INCO foams (among other advantages).
- The screening of numerous different catalysts showed no obvious improvement over carbon-only cathode active materials.
- A polymer-based SPE was successfully developed in order to protect metallic lithium and prohibit dendrite growth. Operational temperature was 70 °C.
- Compatibilization of the porous cathode with the SPE required the partial filling of the cathode porosity with a SPE formulation. Oxygen showed a high permeability in the SPE integration layer (20 000 cc/m².day), which ensured a sufficient availability of oxygen at the active material/SPE interface.
- Lab-cells demonstrated up to 3000 mAh/g and 8 mAh/cm²
- Very low energy efficiency and cyclability was obtained from the cells.
- 800 mAh solid-state Li-air prototypes were successfully developed, based on multiple stacked electrodes and gas distribution channels. They reached similar capacity performances as lab-cells.

Conclusions & Perspectives

From the results of this project, as well as other recent reports, the conclusion is that the technology is still far from being ready for commercialization.

A number of significant challenges remain :

- Establishment of a stable electrochemistry (→ solve the issues related to the chemical instability of Li_2O_2)
- Reach a high energy efficiency (decrease recharge overpotential)
- Use of lithium metal to be further validated (safety concerns)
- Increase the power density by at least an order of magnitude (reaction kinetics)
- System scale-up is far from being obvious, as demonstrated by this work :
 - Gas flow distribution is critical
 - Minimize weight and volume of stack & extra components.
- In case of an open system, find solutions to gas contaminants (H_2O , CO_2 , ...)

Acknowledgements

NRC Boucherville (QC)

- Alexis Laforgue
- Mathieu Toupin
- Asmae Mokrini
- Sean MacKinnon
- Jean-Yves Huot
- Nathalie Raymond
- François Vachon
- Jacques Dufour
- Maxime Gauthier
- Fabrice Bernier
- Mario Laplume
- Florence Perrin-Sarrazin

NRC London (ON)

- Mihnea Ionescu
- Ben Luan

NRC Ottawa (ON)

- Christina Bock
- Michèle Fee
- Svetlana Niketic

NRC Vancouver (BC)

- Xiao-Zi (Riny) Yuan
- Wei Qu
- Ken Tsay
- Max Jiang
- Jason Fahlman

Funding



Natural Resources
Canada

Ressources naturelles
Canada

Vehicle Propulsion Technologies

Innovations to take you further

NRC-CNRC



Thank you !

NRC Booth #1515