First Project Workshop

In Pilsen and Online

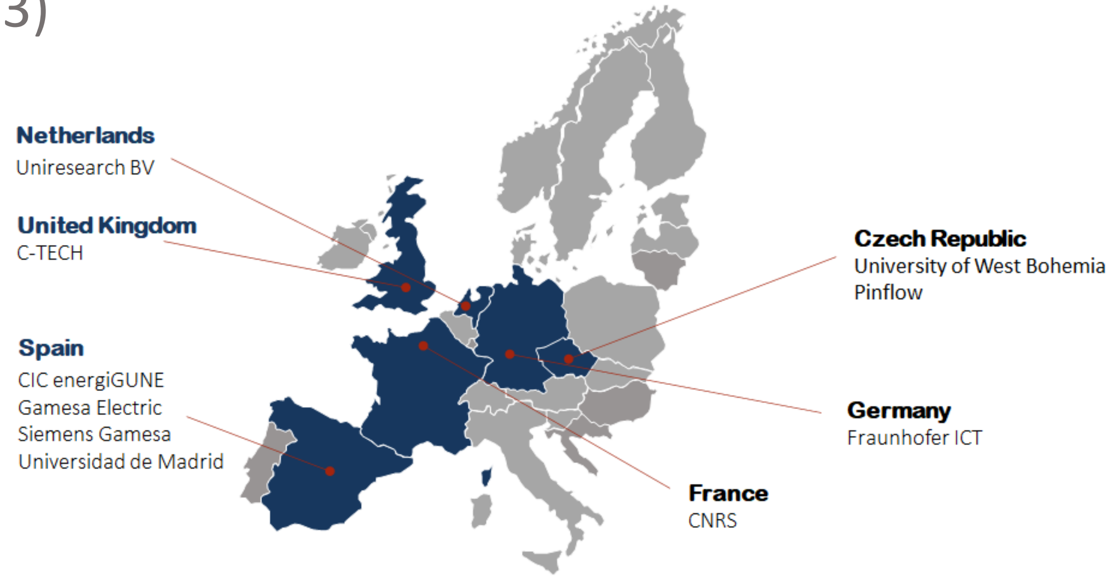
HIGREEW: achievements and hurdles in the deployment of AORFB

Eduardo Sánchez Díez

The research leading to these results has received funding from the European Union under Grant Agreement no. 875613

HIGREEW: Affordable High-performance Green Redox Flow Batteries

- Develop a new generation of redox flow batteries:
  Cost-effective + environmentally friendly + high performance materials
- Duration: 43 months (November 2019 – May 2023)
- Call: H2020-LC-BAT-4-2019
- Total budget: 3,8M€
- 10 partners (6 countries)



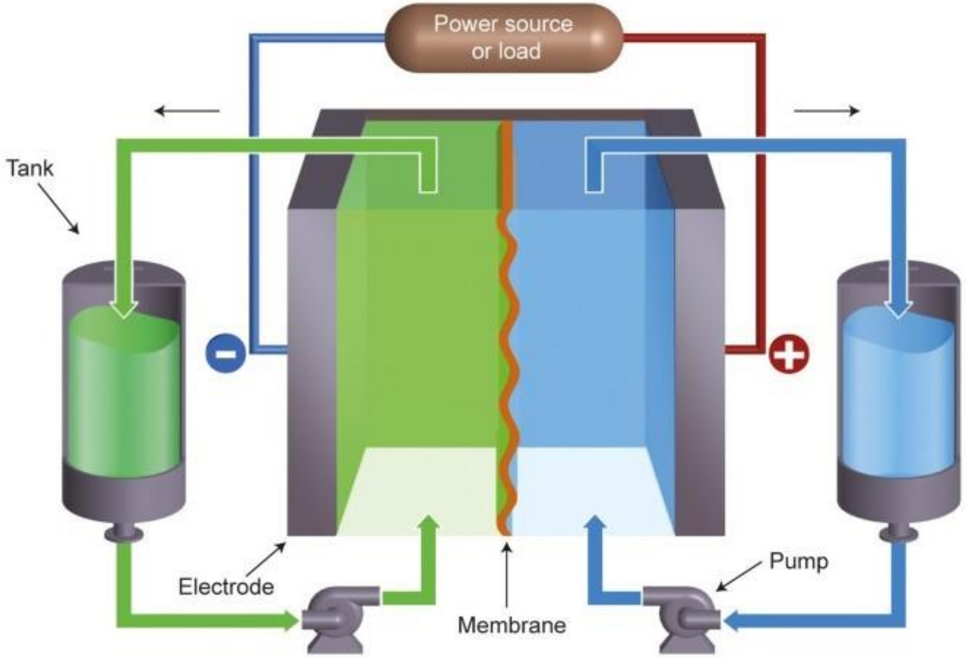
6 Countries

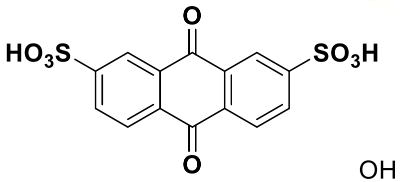
10 Partners
3 R&D Institutes
2 Industrial partners
2 Universities
3 SME

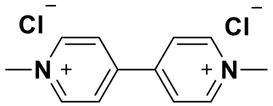
Context – why organic?

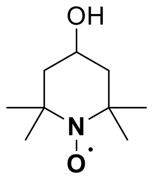
H2020-LC-BAT-4-2019

- Vanadium commercial batteries:
  - Price/scarcity
  - Technical and engineering challenges
    - Corrosive media
    - Temperature
    - Energy density
- AORFB - HIGREEW
  - Earth abundant substances
  - Low cost
  - High tunability









HIGREEW in a nutshell

H2020-LC-BAT-4-2019

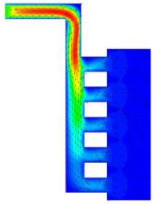
Materials to Prototype

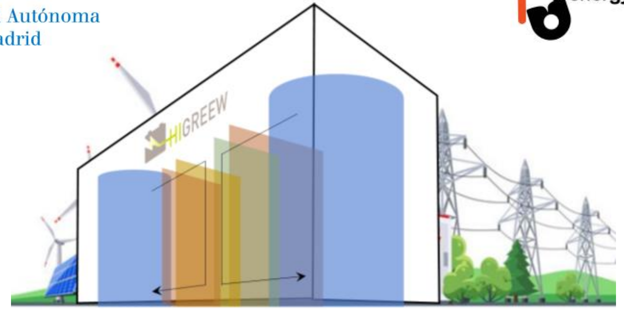
November 2019 – May 2023

WP2: Materials & Cell testing

Innovative materials
Organic active materials
Electrolyte-electrode-membrane

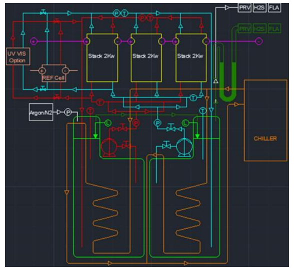
WP3: Stack development





WP1: System

WP4: Prototype



BoP design
Algorithms
Power electronics

WP6: LCA & Safety

LCOS <0,10 €/kWh/cycle

CAPEX
&
OPEX

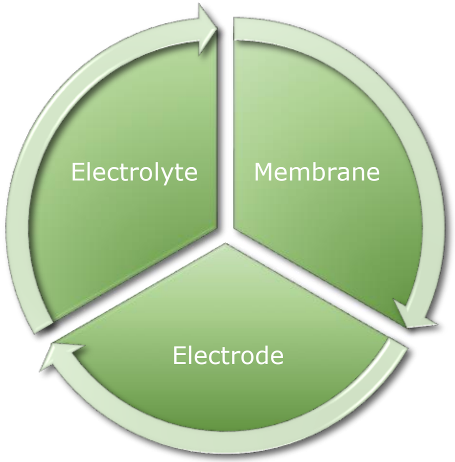
RTE

WP7: Exploitation

WP5: Integration

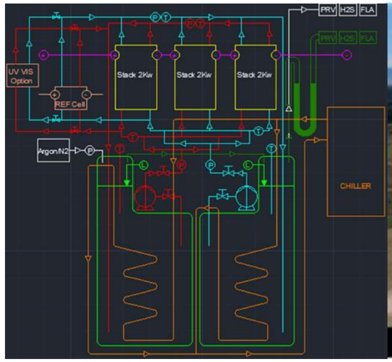
Objectives & Results

Components: material development
Electrolyte-membrane-electrode tandem performance



AORFB cell & stack
New design

AORFB protype
Building & Implementation



Laboratory development | **Up-scaling** | **Prototyping** | **Implementation**

2019 | 2020 | 2021 | 2022 | 2023

Active materials

CIC energiGUNE
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Project proposal/Achievements

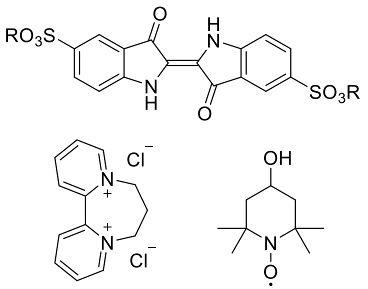
- Design & synthesis of active materials
  - High water solubility
  - High stability

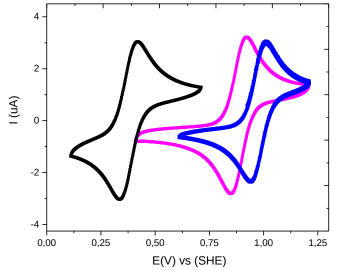
→ Screening: Indigo, viologens, TEMPO & Ferrocyanide derivatives

→ 24 redox active materials synthesized and tested

→ Anode-cathode pairs up to 1,5 V

→ Theoretical capacity up to 72,4 Ah/L





Hurdles

- Upscaling
  - Complex transition from lab to pilot
  - Cost of non-automatized electrolyte production
- Toxicity of reactants or products

Outcome

→ Viologen and ferrocyanide as cost competitive solution (25 €/kWh)

→ NH_4 cation can boost solubility of organic salts as FeCN

→ Viologens highly tunable compounds

→ Modulate toxicity long alkyl chains

→ Modulate Ered & solubility (40 Ah/L)

→ Modulate ionic nature (zwitterionic/cationic/anionic) Conductive CEM

Electrolyte

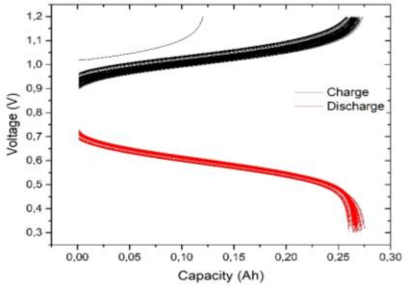
Project proposal/Achievements

- Neutral pH, highly conductive, non-viscous electrolyte
- High energy density and highly stable electrolyte (> 8,000 cycles)

→ Buffered pH 7 electrolytes
> 0,1 S/cm and < 10 cP

→ Stable symmetric and non-symmetric electrolytes for long cycling

→ Charge carrier & supporting electrolyte effect deep studies



Hurdles

- Viscosity
  - Organics molecules confer viscosity to the electrolyte
  - Viscosity increase with SoC
- Neutral pH
  - Low conductivity and low EE
- Robustness of electrolyte
  - Effect of SoC & T

Outcome

→ Stable electrolyte in wide operation window

→ Temperature window (10-45^{o}C)

→ Highly conductive electrolytes based on wise charge carrier selection (> 0,1 S/cm & > 80-125 mA/cm^2)

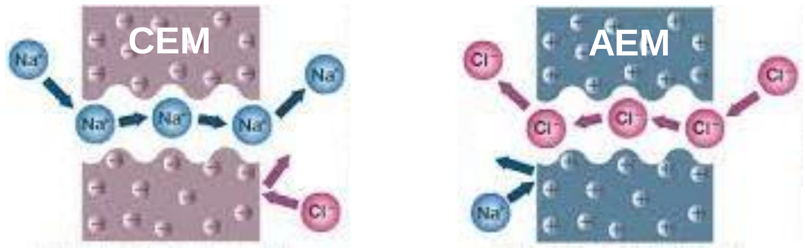
Membrane

Project proposal/Achievements

- Low cost (< 150 €/m^2) durable membranes
- High ionic conductivity (0,5 mS/cm) & low resistance membranes
- Low permeability

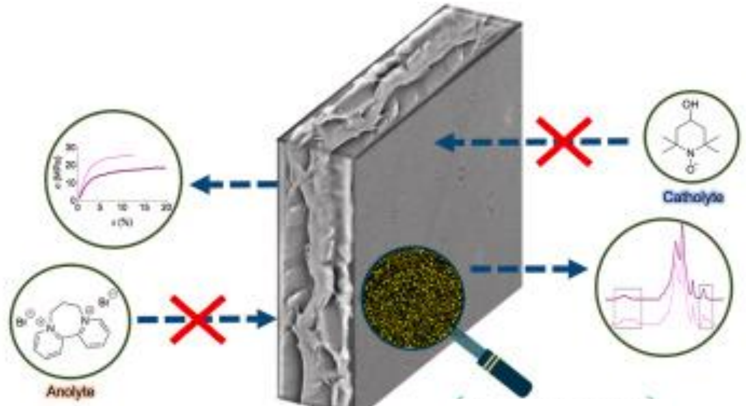
→ Screening of CEM, AEM & porous separators

→ Cost-effective membrane modification strategies



Hurdles

- Resistivity vs cost dilemma
  - Resistive AEM for neutral pH applications
  - High cost perfluorinated CEM
- Crossover in non-symmetric systems
  - Critical long-term crossover



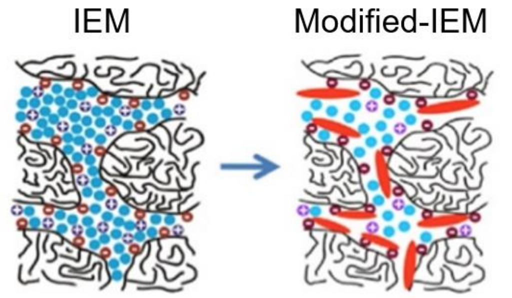
Outcome

→ Low cost membranes with high selectivity

→ Low cost commercial membranes

→ Affordable and scalable processes to minimize crossover

→ PPy in-situ polymerization.
Reduced crossover
Improved mechanical properties



Electrodes

Project proposal/Achievements

- Low cost activation procedures (100 €/m^2) to reach 10^{-3} cm/s kinetics
- Low mass loss / No OER, HER

Activation protocols:
- Thermal activation in CO_2 atm
- Chemical activation HNO_3
- Mixed activation thermal/chemical

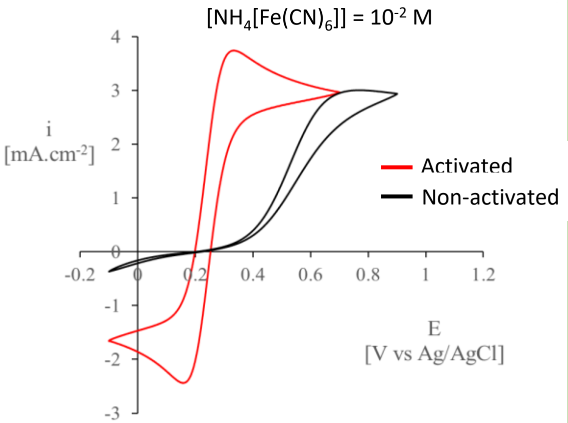
Evaluated with micro-fiber electrodes (extracted from activated carbon felts) to calculate k^0

Plotting and modelling of cyclic voltammetry and impedance spectroscopy

Hurdles

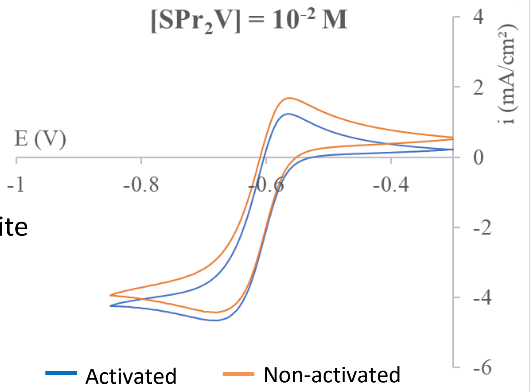
- Particularity of each redox pair
  - Ferrocyanide

WE = µfiber
RE = Ag/AgCl wire
CE = graphite com
v = 100 mV/s



  - Viologen

WE = µfiber
RE = Ag/AgCl wire
CE = graphite composite
v = 100 mV/s
In glove box



Outcome

New characterization method to determine kinetics and cost-effective activation for anolyte/catholyte

EIS / CV combination
Micro-fiber analysis

Activation improves the electrochemical performance of ferrocyanide

k^0 increases from 10^{-5} to 10^{-3} cm/s

Viologen not impacted by activation: kinetics already fast on non-activated material

k^0 around 10^{-2} cm/s

Cell & stack design

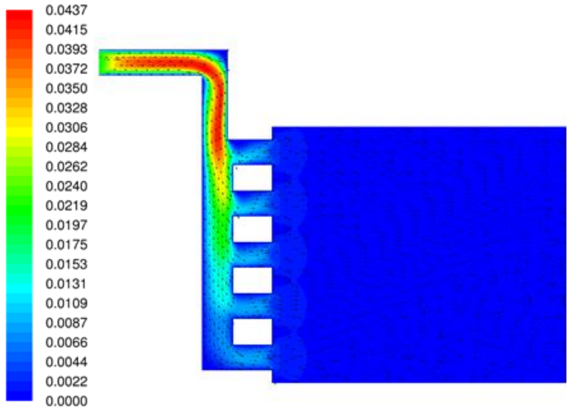
Project proposal/Achievements	Hurdles	Outcome

Project proposal/Achievements

- Low cost stack at MW scale
  - High RTE
  - Easy assembly/disassembly
  - Low shunt currents (< 1% CE losses)

→ Novel assembly strategies
Novel sealing methods

→ CFD modelling and cell design
Shunt currents analytical model



Hurdles

- AORFB database at prototype level
- Variable properties of electrolyte
  - f(T)
  - f(SoC)
  - Long term composition change
- Different properties in each half-cell
  - Viologen higher viscosity than FeCN

Outcome

→ Experimental-computational characterization of AORFB at stack level to reach high RTE

→ Conventional vs Non-symmetric cell designs

→ Compatibility of materials to new chemistries

→ Adapted BP designs to balance anolyte/catholyte viscosity differences

→ Flow distribution studies for different cell geometries for AORFB

Algorithms

Project proposal/Achievements	Hurdles	Outcome

Project proposal/Achievements

- ❖ Efficient, safe & autonomous prototype that can adapt to operation promoted changes
  - ❖ Temperature, SoC, Pressure

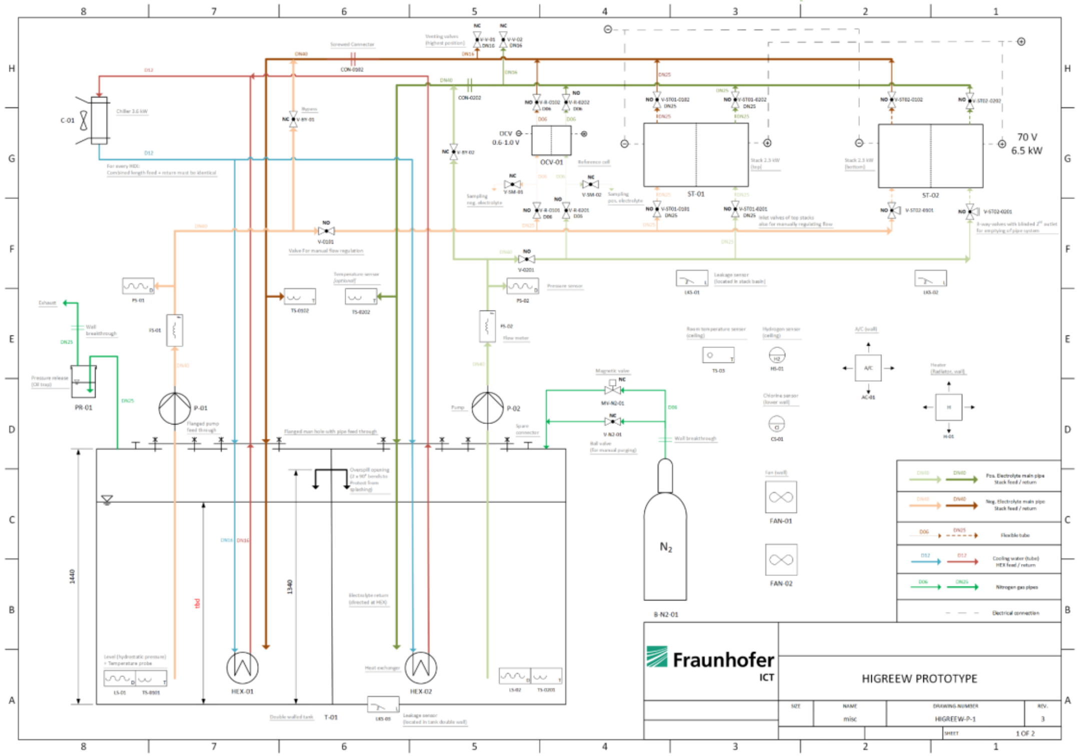
Algorithms developed in Matlab for implementation in PLC to control a number of variables (T, P, SoC) through sensors and corresponding actuators (cooling/heating system, pumps, etc.)

Hurdles

- ❖ Lab to prototype characterization gap

Outcome

Safe system for operation in real conditions able to adapt to operation and external conditions



Sensors: T, P, flowmeters, leakage, gases

Actuators: Pumps, fans, chiller, heater

Battery management

Pressure control strategies

BoP

Project proposal/Achievements

- Functional 5kW/20kWh AORFB prototype to implement in Renewables plant

Develop a fully functional prototype with all safety measures for implementation in real scenario

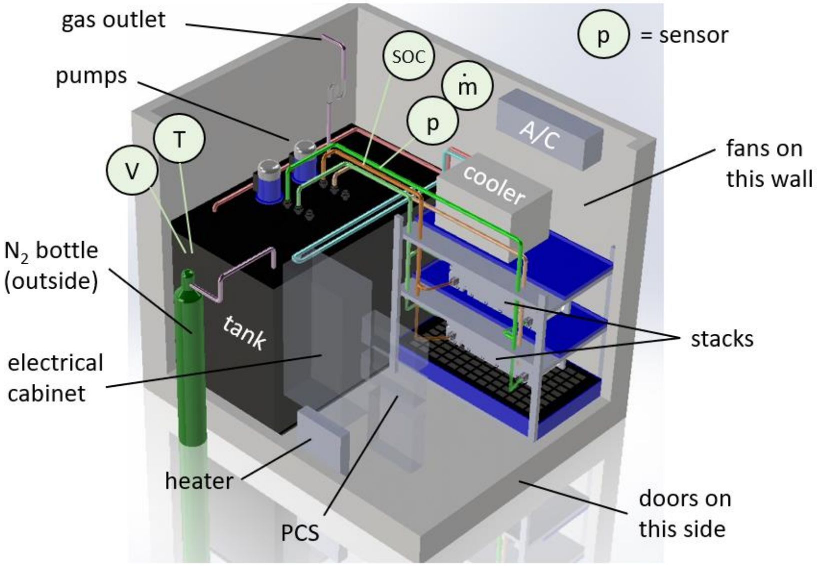
BoP design and risk analysis HAZOP performed

Hurdles

- Building BoP for new chemistry
  - Components including sensors shall adapt to chemical requirements
  - Different electrochemistry means different power electronics (neutral pH, polarization)
- Uncertainties in long term behaviour. Forecast changes and needs in advance.

Outcome

Functional prototype for operation in renewables plant able to operate under safe conditions and characterize the system for efficiency evaluation



Final remarks & Next steps

Laboratory development	Up-scaling	Prototyping	Implementation

2019 | 2020 | 2021 | 2022 | 2023

- Materials development stage has concluded with success finding innovative cell component
- Stack design and building are ongoing and will require materials developers support
- Prototype building is ongoing
- LCA, LCOS & Safety analysis will ramp up for this final stage as components/designs get more concrete
- Time to boost dissemination and share results with community

Thank you!

The research leading to these results has received funding from the European Union under Grant Agreement no. 875613

Disclaimer/ Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 875613. The information and views set out in this publication does not necessarily reflect the official opinion of the European Commission. Neither the European Union institutions and bodies nor any person acting on their behalf, may be held responsible for the use which may be made of the information contained therein.