HERON: Nanoconfined ionic liquids on porous carbons as electrocatalysts for the electrochemical production of NH_3: computational and experimental evidences

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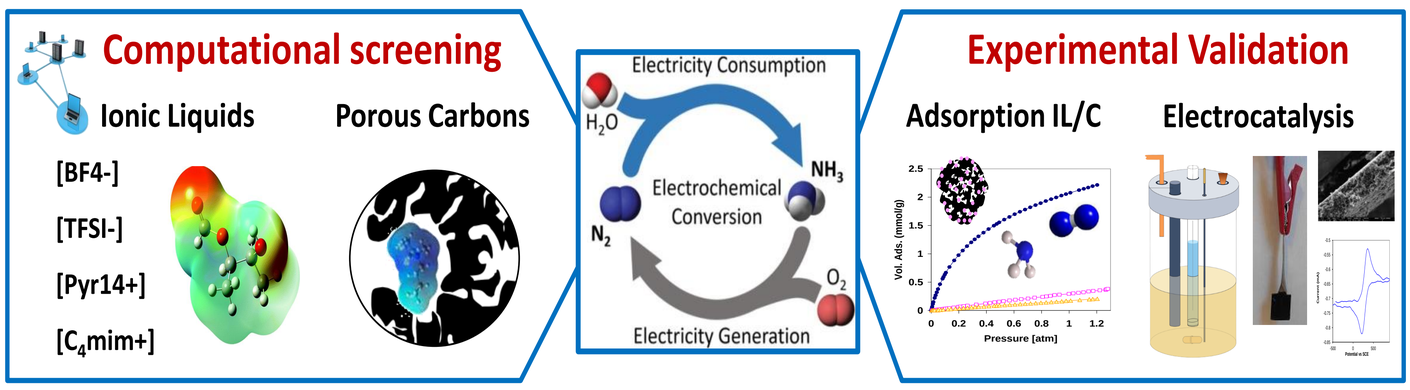
The goal of **HERON** is to combine experimental and computational approaches for an screening of the best suited ionic liquids for their confinement in porous carbons with well defined pore architectures in the full nanopore range. The objective is to identify the best candidates IL-carbon to be tested in the electrochemical reduction of nitrogen to produce ammonia in lab-scale electrochemical reactors in gas/liquid phase.

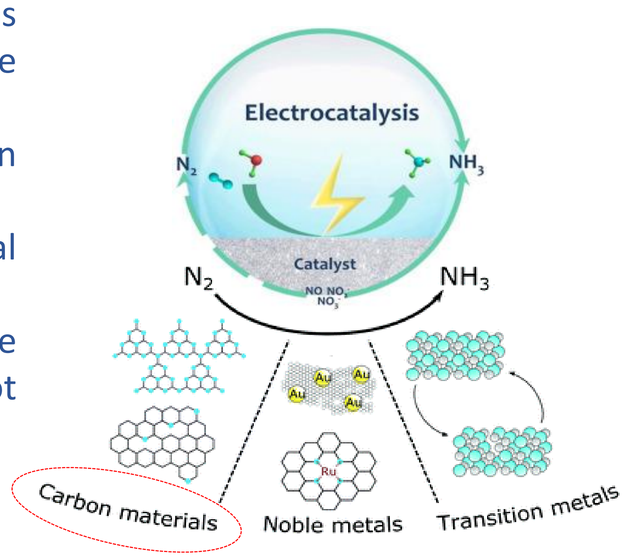
Computational studies allowed to analyze IL with varied cation-anion combinations, to identify the characteristics that define interactions with N_2 molecules. The best candidates identified in the computational screening were tested experimentally to:

1) validate the enhanced adsorption/solubility of N_2 gas in carbon materials with controlled pore characteristics and

2) demonstrate the validity of the approach in the electrochemical Nitrogen Reduction Reaction (NRR).

The novelty of **HERON** lies in the use of immobilized in a metal-free porous carbon catalyst (as a second component of catalyst) and not as electrolyte.





N≡N: high bonding energy (945 kJ mol^{-1}), high ionization potential (15.8 eV), negative electron affinity (−1.9 eV), and low solubility in water (0.68 mM at 1 atm, 25ºC). All this limits the NRR (thermodynamically and kinetically)

Electrochemical NRR

$$N_2 + 6H^+ + 6e^- \rightarrow 2\,NH_3$$
$$N_2 + 6H_2O + 6e^- \rightarrow 2\,NH_3 + 6OH^-$$

Competing cathodic reaction (HER)

$2H^+ + 2e^- \rightarrow H_2$ (fast)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (sluggish)

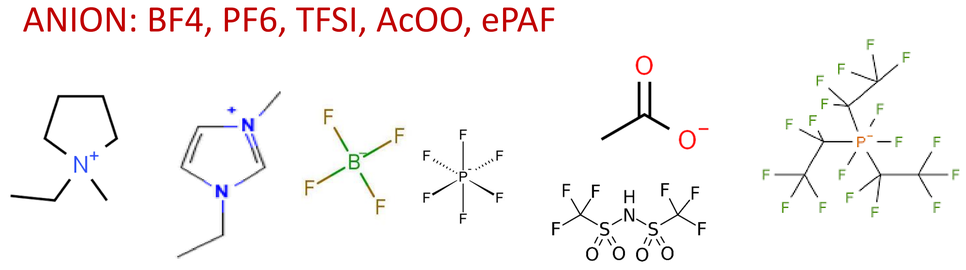
(less e- involved..... kinetically favored)

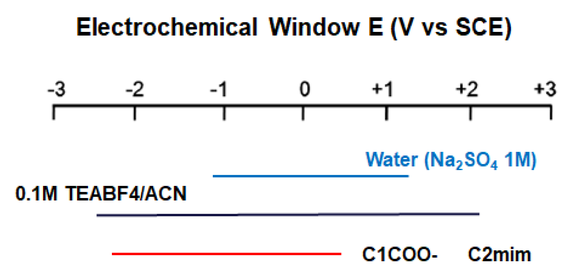
HERON Results

Screening of ILs: DFT analysis of N_2-IL interactions; N_2 solubility; electrochemical window

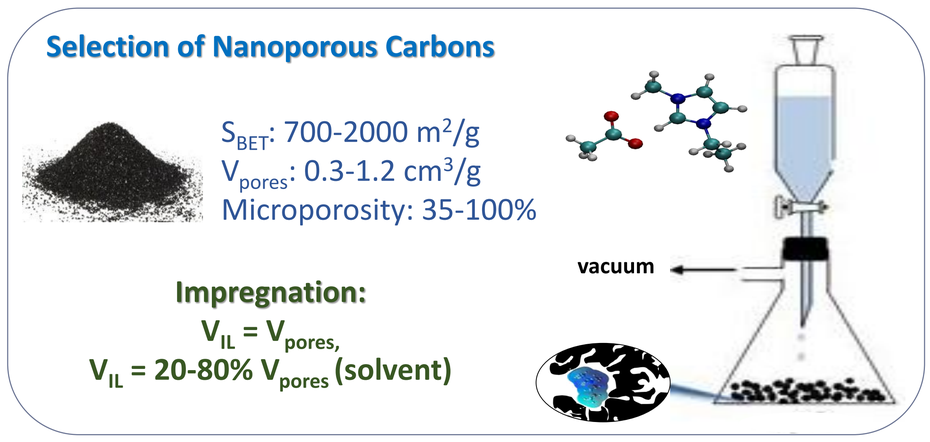
CATION: [C2/C4]-1-pyrrolydinium / -3-methyl-imidazolium

ANION: BF4, PF6, TFSI, AcOO, ePAF





Selection of Nanoporous Carbons



S_{BET}: 700-2000 m^2/g

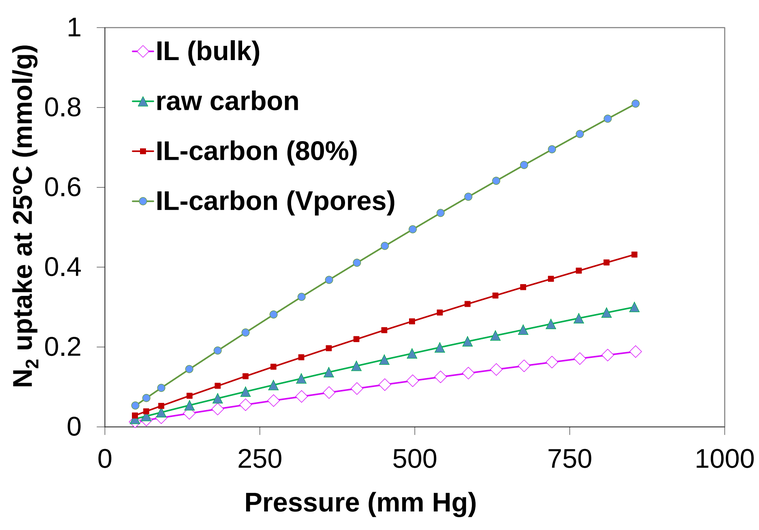
V_{pores}: 0.3-1.2 cm^3/g

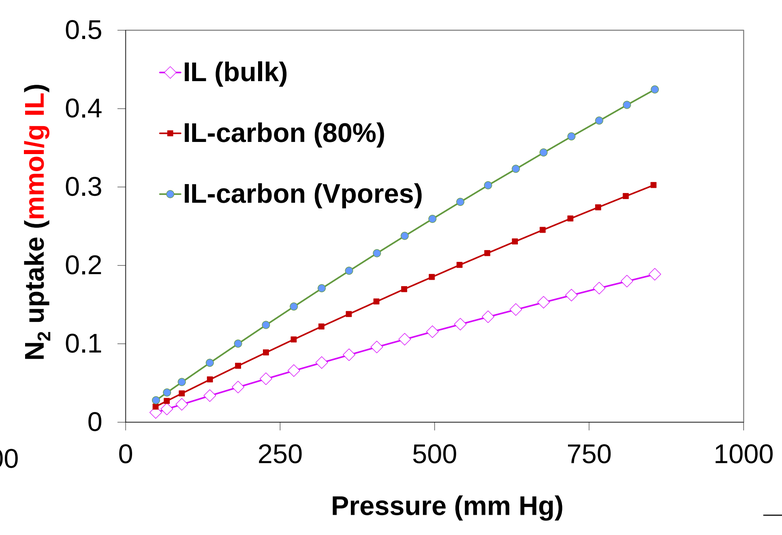
Microporosity: 35-100%

Impregnation:

$V_{IL} = V_{pores}$,

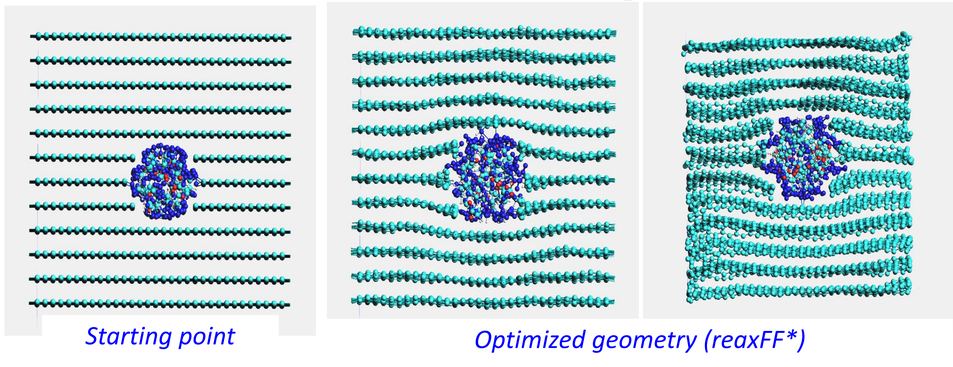
V_{IL} = 20-80% V_{pores} (solvent)





slit-shape graphitic pores (1-2.5 nm) in 4x4x4 nm^3 cell

1 nm pore + C2mIm + N_2

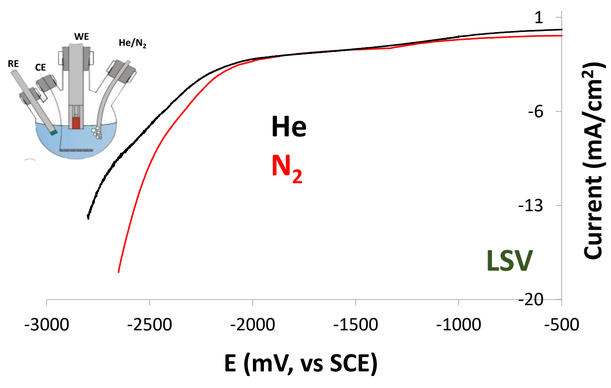


Starting point — *Optimized geometry (reaxFF*)*

*Spicher et al. Angew. Chem. Int. Ed. 59 (2020) 15665

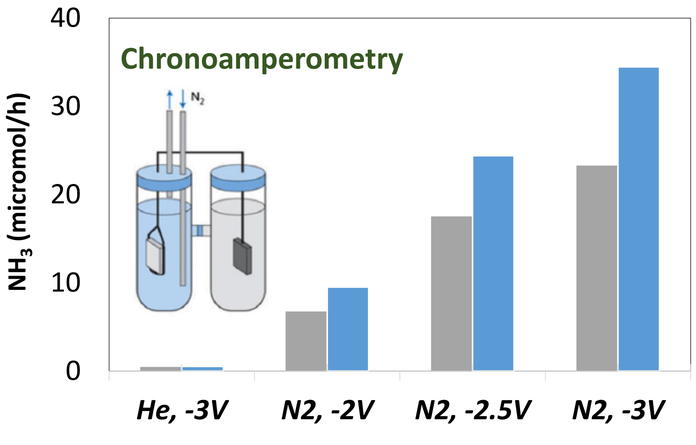
N_2@25ºC	N_2 uptake (cm^3/g composite)	N_2 uptake (cm^3/g CARBON)	N_2 uptake (cm^3/g IL)
AC (raw)	--	11	--
AC/IL-80%	28	19	6
AC-IL-100%	33	37	8
IL bulk	--	--	4

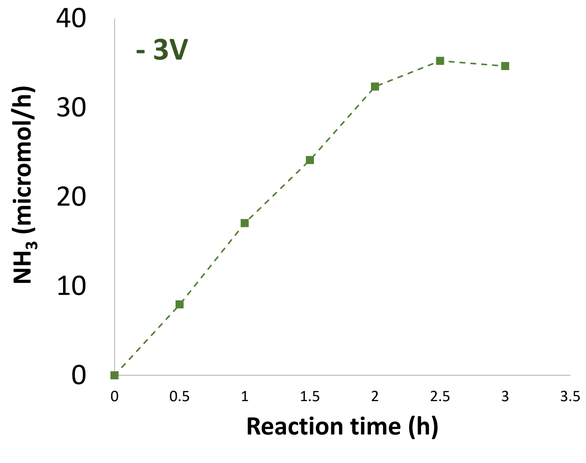
Electrochemical NRR Screening



Linear Sweep Voltametry (LSV) screening of the carbon/IL electrodes in He and N_2 atmosphere

Amount of NH_3 electrogenerated upon chronoamperometry at various potentials and kinetics of the electrocatalytic NRR at -3V





HERON Outcome and Perspectives

The electrocatalytic activity of carbon/IL for the reduction of N_2 into NH_3 has been demonstrated. Even though faradaic efficiency and NH_3 production yield still need to be improved, this opens up new perspectives for the electrochemical production of NH_3 from a wide variety of N-sources (e.g., N_2, NO_3^-, NO_2^-) using low-cost carbon electrocatalysts without non-noble metals.

Combined experimental and computational approaches have demonstrated the N_2/carbon/IL interactions as responsible for the increases uptake of N_2 gas inside the nanopores of carbons impregnated with IL.