Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information

to accompany

Sustainable Nitrogen Activation – Are we there yet?

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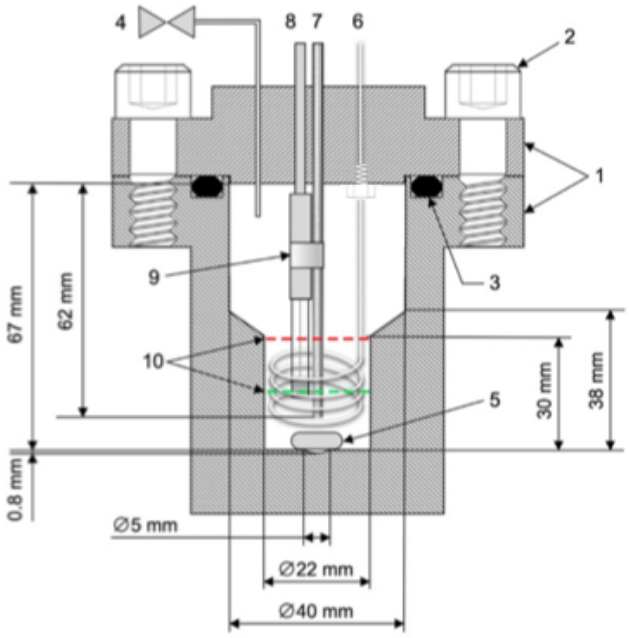
1. Elevated Pressure Electrochemical Cell Design

This design was published as part of Du et al (DOI: 10.1038/s41586-022-05108-y). The update shown here includes a threaded section and nut on feedthrough 6 that ensures that the feedthrough can never be expelled under pressure. Broadly, all of the feedthroughs 4,6,7,8 should be designed in such a way that ejection under pressure cannot take place.



2. DFT Computational Details.

The mechanism for the N_2 adsorption and splitting on bcc Li(001), also equivalent to (010) and (100) surfaces, has been studied by means of density functional theory (DFT) through the generalised gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof (RPBE) functional with Pade approximation, using plane-wave cut-off energy of 400 eV. The Brillouin zone (periodic boundary conditions) was sampled by 3×3×1 *k*-points using the Monkhorst-Pack scheme. In order to avoid interactions between periodic slabs, a vacuum width of 15 Å was imposed. Optimisation calculations were done using energy and force convergence limits equal to 10^{-4} eV/atom and |0.01| eV/Å, respectively. Explicit dispersion correction terms to the energy were also employed using the D3 method with the standard parameters programmed by Grimme and co-workers. Transition states were located using the improved DIMER method (IMD). Free energies have been calculated for gases and adsorbates, although ultimately due to the strong capture of N_2 on Li, the vibrational modes of the Li and N atoms

were not considered. All optimisation and vibrational frequency calculations have been performed throughout the facilities provided by the Vienna *Ab-Initio* Simulation Package (VASP, version 5.4.4). The results shown here are broadly consistent with the calculations of Ludwig et al J. Phys. Chem. C 2020, 124, 26368−26378.