CoCrFeMnNi HIGH-ENTROPY ALLOYS FOR LITHIUM-MEDIATED ELECTROCHEMICAL NITROGEN REDUCTION

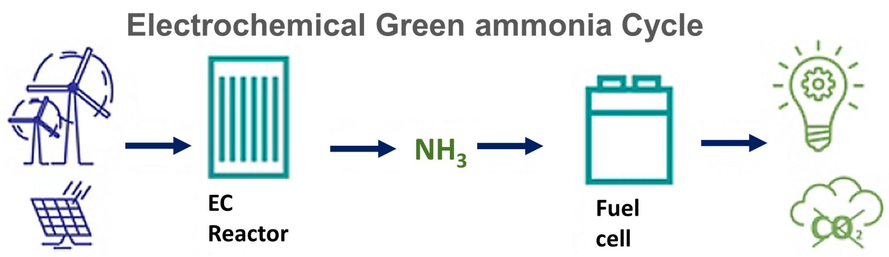
Jakob Thyr[a], Rafael Araujo[a], Robin Dürr[a], Esat Pehlivan[b], León Zendejas Medina[c], Tomas Kubart[d], Ilknur Bayrak Pehlivan[a], Tomas Edvinsson[a,e]

[a] Department of Materials Science and Engineering, Solid State Physics, Uppsala University – Uppsala, Sweden
[b] Department of Physics and Astronomy, FREIA, Uppsala University – Uppsala, Sweden
[c] Department of Chemistry-Ångström laboratory, Inorganic Chemistry, Uppsala University – Uppsala, Sweden
[d] Department of Electrical Engineering, Solid-State Electronics, Uppsala University – Uppsala, Sweden
[e] Energy Materials Laboratory, School of Natural and Environmental Science, Newcastle University – Newcastle, United kingdom

ABSTRACT: Ammonia is a promising energy vector and can be used as a hydrogen storage medium. Electrocatalytic ammonia syntheses using renewable energy are attractive low-temperature options to the Haber-Bosch high-temperature process, which releases CO_2 in the atmosphere and contributes to the greenhouse effect. High-entropy (HEA) alloys belong to a new class of materials that can provide single-phase stabilizations by mixing different species and are promising candidates to overcome scientific challenges posed by electrochemistry. Lithium-mediated ammonia synthesis is a way to get high-performance ammonia electrosynthesis from nitrogen at room temperature. In this work, we investigated lithium- mediated ammonia synthesis of a thin-film high-entropy catalyst of CoCrFeMnNi.

MOTIVATION

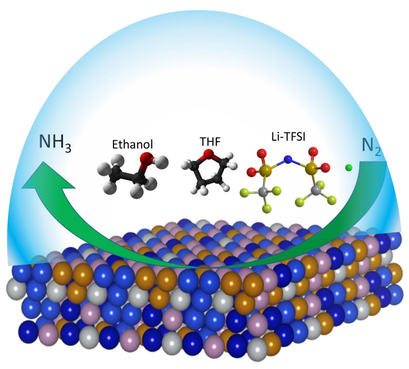
Ammonia is a potent hydrogen storage carrier.



Lithium mediated electrocatalytic ammonia synthesis[a]

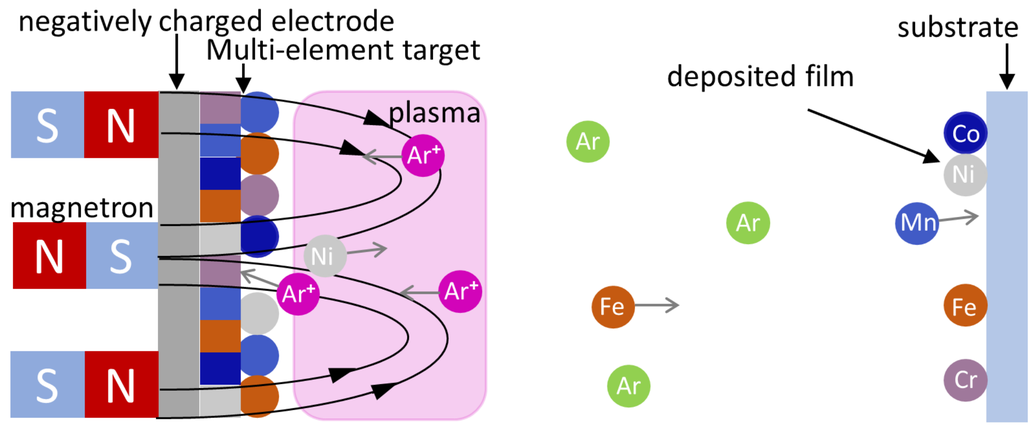
$$Overall\ reaction: \quad 3\,Li^+ + 1/2\,N_2 \underset{-3\,B^-}{\overset{3\,e^-}{\rightleftarrows}} Li_3N \xrightarrow{3\,BH} 3\,Li^+ + NH_3$$

High-entropy alloys - A new class of materials that provides single-phase stabilization via entropic effects by mixing different species. HEAs are alluring for catalytic applications due to their increased potential for tuning the catalytic properties by regulating the composition and elements contributing to catalytic activity, selectivity, and stability.

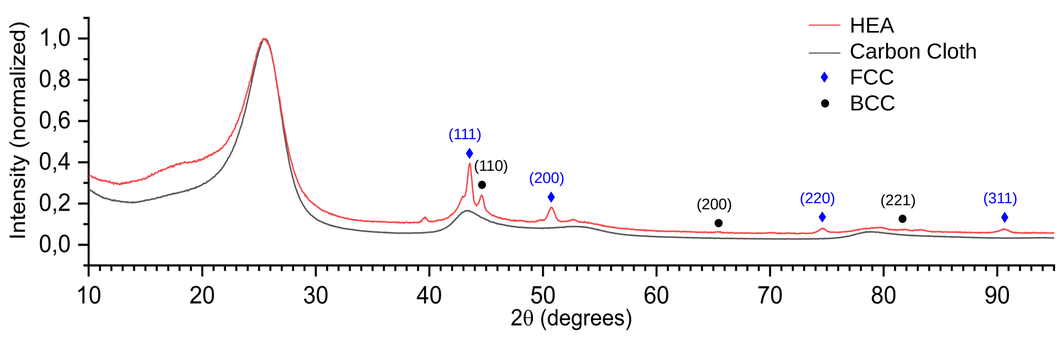


METHODS & CHARACTERISATION

Thin film coating: DC magnetron sputtering

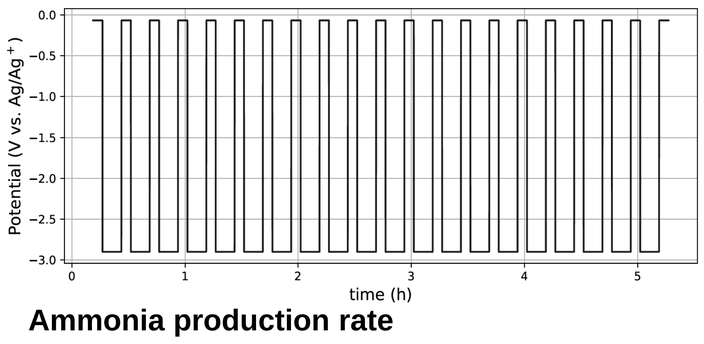


Characterization of CoCrFeMnNi films with XRD



RESULTS

Pulsed chronoamperometry



Ammonia production rate

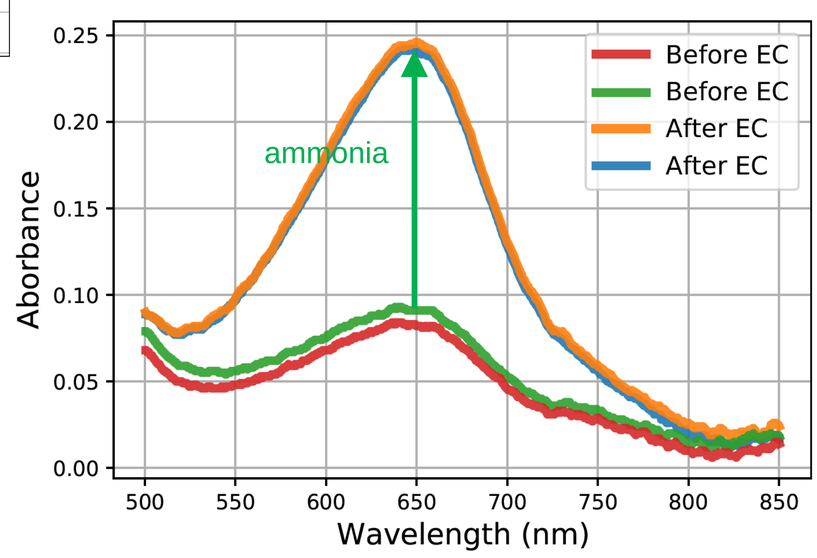
$$R_{NH_3}(mol \cdot cm^{-2} \cdot s^{-1}) = \frac{x(ppm) \times 10^{-3}\left(\frac{g}{mg}\right) \times V(L)}{Mr_{NH_4^+}\left(\frac{g}{mol}\right) \times t\,(s) \times S(cm^2)}$$

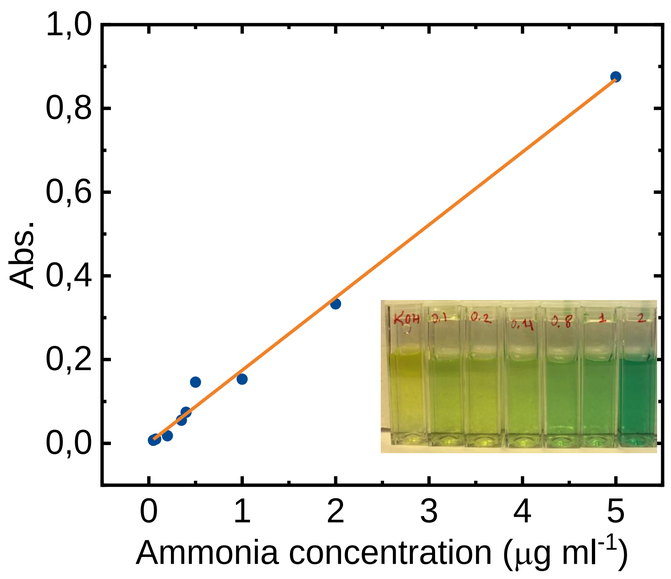
Faradic efficiency

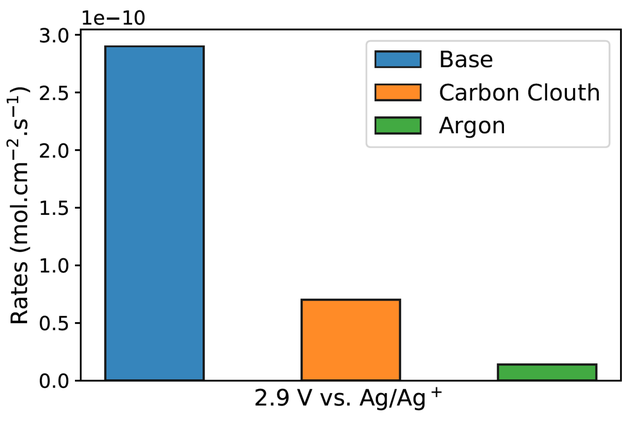
$$FE(\%) = \frac{3F \times R_{NH_3}}{I}$$

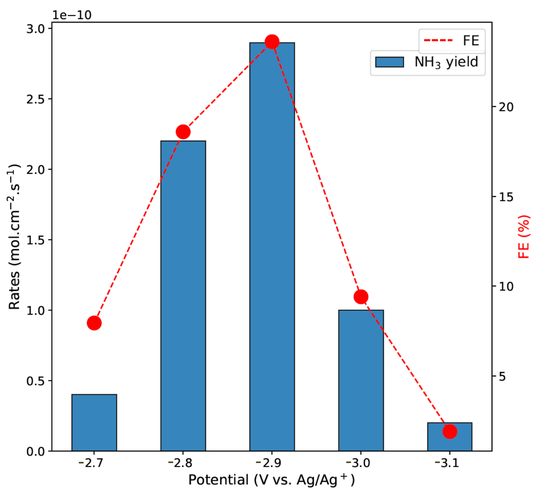
x : the ammonia concentration in the electrolyte
V : the volume of the electrolyte
$Mr_{NH_4^+}$: the molecular weight of NH_4^+
t : the reaction time
S : the geometric area of the electrode
I : the average current density during the experiment.
F: the Faraday constant

Determination of ammonia production: Indophenol blue method









CONCLUSIONS

Ammonia production was evaluated by performing a series of electrochemical measurements in the electrolyte of 2 M LiTFSI in tetrahydrofuran (THF) and 1 vol% of ethanol. The measurements were done in a single cell using CoCrFeMnNi HEA catalysts coated on carbon cloth, a Pt counter electrode and a Ag/Ag^+ reference electrode. The lithium mediated nitrogen reduction reactions were performed at different potentials and temperatures. Ammonia production rate of $2.9 \cdot 10^{-10}$ mol cm^{-2} s^{-1} was achieved at -2.9 V under ambient conditions using pulsed chrono-amperometry. The pulsed potential was needed to counteract surface poisoning. The study shows that electrochemical nitrogen reduction is possible at ambient conditions.

ACKNOWLEDGEMENT

The TELEGRAM project has received funding from the European Union's Horizon 2020 Research and Innovation programme under grant agreement No 101006941.

MORE INFORMATION: jakob.thyr@angstrom.uu.se

a Schwalbe, Jay A., et al. "A Combined Theory-Experiment Analysis of the Surface Species in Lithium-Mediated NH_3 Electrosynthesis." *ChemElectroChem* 7.7 (2020): 1542-1549.