

Efficient electrocatalytic reduction of nitrogen at iron phosphide catalysts

Beata Rytelawska¹, Anna Chmielnicka¹, Takwa Chouki², Shaghayegh Naghdi³, Dominik Eder³, Saim Emin², Iwona A. Rutkowska¹, Pawel J. Kulesza¹

¹*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

²*Materials Research Laboratory, University of Nova Gorica, Ajdovscina 5270, Slovenia*

³*Technische Universität Wien, Institut für Materialchemie, Getreidemarkt 9, 1060, Vienna, Austria*

**b.rytelawska@uw.edu.pl*

Industrial-scale NH₃ production mainly relies on the energy-consuming Haber–Bosch process operating at high temperature (400–500 °C) and pressure (200–250 bar) with N₂ and H₂ as feeding gases. The electrochemical N₂ reduction reaction performed under ambient condition with water as hydrogen source has been proposed as a sustainable alternative solution for ammonia production, especially when it is powered by electricity from largely distributed renewable energy sources such as solar and wind. The big challenge is to develop cost effective electrocatalysts capable of converting N₂ to NH₃ in high yield and Faradaic efficiency, thus enabling the mass production of ammonia. The feasibility of pursuing nitrogen electroreduction reaction, or nitrogen fixation, particularly in aqueous solutions, constitutes an attractive prospect to produce ammonia under ambient, or near ambient, conditions. Development of durable, specific and reasonably efficient low-cost catalysts remains a great challenge for electrochemical science and technology. Currently, most of electrochemical approaches to N₂-fixation suffers from slow kinetics due to the difficulty of achieving the appropriate adsorption and activation of dinitrogen leading to cleavage of the strong, triple N≡N bond.

A catalytic system based on iron phosphide (Fe₂P) has exhibited electrocatalytic activity toward N₂-reduction reaction in alkaline (NaOH) and semi-neutral (phosphate buffers) media. Based on voltammetric stripping-type electroanalytical measurements, Raman spectroscopic and spectrophotometric data, it can be stated that the Fe₂P catalyst facilitates conversion of N₂ to NH₃, and the process is fairly selective with respect to the competing hydrogen evolution. A series of diagnostic electrocatalytic experiments (utilizing platinum nanoparticles and HKUST-1) have been proposed and performed to control purity of nitrogen gas and to probe presence of potential contaminants such as ammonia, nitrogen oxo-species and oxygen. On the whole, the results are consistent with the view that the interfacial reduced-iron (Fe⁰) centers, while existing within the network of P sites, induce activation and reduction of nitrogen, parallel to the water splitting (reduction) to hydrogen. It is apparent from Tafel plots and impedance measurements that mechanism and dynamics of nitrogen reduction depends on the applied electroreduction potential. The catalytic system exhibits certain tolerance with respect to the competitive hydrogen evolution and gives (during electrolysis at -0.4 V vs. RHE) the Faradaic efficiency, namely, the selectivity (molar) efficiency, toward production of NH₃ on the level of 60%. Under such conditions, the NH₃-yield rate has been found to be equal to 7.5 μmol cm⁻² h⁻¹ (21 μmol m⁻² s⁻¹). By referring to classic concepts of electrochemical kinetic analysis, the rate constant in heterogeneous units has been found to be on the moderate level of 1-2*10⁻⁴ cm s⁻¹ (at -0.4 V). The above mentioned iron-phosphorous active sites, which are generated on surfaces of Fe₂P particles, have also been demonstrated to exhibit strong catalytic properties during reductions of other electrochemically inert reactants, such as oxygen, nitrites and nitrates.

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