A Versatile Method for Ammonia Detection in a Range of Relevant Electrolytes via Direct Nuclear Magnetic Resonance Techniques

Electrocatalytic N-2 reduction to ammonia has recently attracted a great deal of interest as a possible renewable energy-driven alternative to the Haber-Bosch process. However, the detection of NH3 after attempting electrocatalytic reduction of N-2 can be hampered by low NH3 yields, ambient NH3 contamination, and the need for multistep chemical separation of NH3 from the electrolyte. Herein, we report a frequency-selective pulse nuclear magnetic resonance (NMR) method and quantify the efficacy of this method to measure the concentration of NH3 (present in the assay as NH4+) in an electrolyte after electrocatalysis. This NMR method was demonstrated to be effective in a variety of nondeuterated, nonaqueous and aqueous electrolytes, and did not require the separation of NH3 from the electrolyte. NH3 sensitivity down to 1 μM was readily achieved with isotopic and chemical specificity. Compatible electrolytes and solvents included ethanol, tetrahydrofuran, dimethyl sulfoxide, acetonitrile, propylene carbonate, diethyl ether, hexanes, and water. The efficacy of the commonly employed Berthelot method was also quantified and compared to the NMR method in a range of nonaqueous and aqueous electrolytes, including ethanol, THF, propylene carbonate, and water.