An approach to Electrochemical Ammonia synthesis using Concentrated Electrolytes

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The Haber-Bosch process (HBP) is undoubtedly one of the most important inventions of the 20th century. An industriallevel ammonia production has helped to sustain global population growth. Yet, its drawbacks, notably the substantial energy demand and carbon footprint, loom large in the contemporary context of climate change and global warming. Consequently, there's a pressing demand for an energy-efficient and carbon-neutral alternative for ammonia synthesis. Two primary avenues of exploration have emerged: electrochemical nitrogen reduction (ENRR) to ammonia and photocatalytic ammonia synthesis. Additionally, efforts are underway to develop a "green" variant of the HBP, where ammonia is synthesized using green hydrogen at lower temperatures and pressures. Our research primarily focuses on electrochemical nitrogen reduction to ammonia at ambient conditions. Although the reaction (Equation 1) is sluggish and poorly selective towards ammonia, many catalysts have been developed and tested for ENRR to improve the rate of ammonia formation and efficiency. However, there's a noticeable gap in research concerning electrolytes. This research narrows down on electrochemical nitrogen reduction to ammonia with Water in salt-type electrolytes of CaBr₂ and MgBr₂. Their high solubility for nitrogen gas, which was tested and shown higher value compared to aqueous electrolytes, and low water concentration due to the formation of solvated ions is expected to show improved ammonia formation rate and Faradaic Efficiency. Also, at the anode, the oxidation of bromide to bromine, which occurs at a lower potential than that of water oxidation, helps to reduce the anodic potential. Preliminary results with Pt: Ru (1:1)¹ alloy as the catalyst have shown improved rate and efficiency compared to the catalytic activity in aqueous electrolytes with a maximum rate of 80.52 µg h⁻¹cm⁻² at -0.35 V vs RHE and a maximum Faradaic Efficiency of 13.72% at -0.15 V vs RHE. Further optimization and expanding studies into other concentrated electrolytes and better catalysts will pave the way for a better rate of ammonia formation and Faradaic Efficiency.

 $N_{2(g)} + 6H^+ + 6e^- \longrightarrow 2NH_{3(aq)}$ $E^0 = 0.092 V vs RHE$ (1)

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References:

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