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Ionic Liquids for Ammonia Electrosynthesis and Energy Storage

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Ammonia has many attributes that make it the ideal energy storage compound. The feedstocks are plentiful, ammonia is easily liquefied and routinely stored in large volumes in cheap containers, and it has exceptional energy density for grid-scale electrical energy storage. Indeed, because of the high energy density and low reactivity of ammonia, the capital cost for grid storage will be lower than any other storage application.[1, 2]

While ammonia is made naturally from biological processes and industrially from Haber-Bosch, these processes are not suitable for energy storage. For the highest energy storage density, chemical bonds are required which can be formed from and be converted back to electricity. The electrochemical synthesis of NH_3 provides the most direct and theoretically most efficient process to do this (eq. 1):

$$N_2 + 6e^- + 6H^+ \rightarrow 2NH_3 \quad (1)$$

DFT calculations by Norskov *et al.* predict that ammonia can be electrochemically synthesized at room temperature on Ru surfaces if protons are supplied at sufficiently negative potentials and hydrogen evolution is suppressed.[3] The ammonia formation reaction can only occur in the absence of site-blocking adsorbates such as water or oxygen since they are a poison for NH_3 catalysts. Marnellos *et al.* demonstrated the electrochemical synthesis of ammonia from H_2 and N_2 using high-temperature proton conductors at atmospheric pressures.[4] However, though they reported that >78% of their electrochemically-pumped H_2 was converted to NH_3, they were limited by very low proton conductivity at 570°C.

In fact, in order to get electrochemical NH_3 production at greater rates, there is a pressing need to use electrolytes that show greater proton transport at reduced temperatures. Ideally, the temperature range should be high enough for fast kinetics and low enough to reduce NH_3 decomposition, which can greatly enhance the viability of the electrochemical production of NH_3.

The work we are presenting involves the synthesis and characterization of anhydrous, proton-conducting ionic liquids (IL) that can operate from 100 to 400°C. Different anions have been studied including benzimidazolates and phosphonates, both of which have been shown to be proton conducting and hydrophobic. These ionic liquids have been prepared as pure and mixed ILs to improve upon the proton conductivity and hydrophobicity of earlier work, and their properties characterized.

As nitrogen is converted to ammonia, the protic ionic liquid will immediately capture the ammonia as solvated ammonium ions. Kinetically this will likely happen quickly, but will depend on the solubility of the ammonia in the IL, and the equilibrium constant of the ammonia protonation reaction in the ILs (eq. 2):

$$NH_3 + H^+ \text{<-->} NH_4^+ \quad (2)$$

As a consequence, the conductivity of the IL will change, which will greatly affect the production rate of the ammonia electrosynthesis process.

Accordingly, we have designed and built a new electrochemical system able to characterize ILs in a wide range of pressures (0 – 3,000 psi) and temperatures (-30 – 400 ºC) as well as ammonia concentrations. Figure 1 shows an schematic representation of the electrochemical cell included in the system.

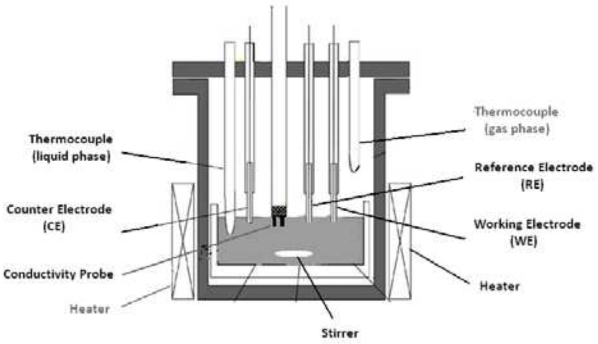

Figure 1. Schematic representation of the electrochemical cell used in the electrochemical system design for operation in a wide range of pressures (0 – 3,000 psi) and temperatures (-30 – 400 ºC)

Conclusions

We have characterized anhydrous, proton-conducting ionic liquids using a newly designed and built electrochemical system able to operate in a wide range of pressures (0 – 3,000 psi) and temperatures (-30 – 400 ºC). As a result, we have been able to determine electrochemical properties of ILs at different pressures, temperatures and ammonia concentrations as well as track the ammonia electrosynthesis process.

Acknowledgement

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References

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