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TRANSFORMATION OF WASTE NO_X TO AMMONIA

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BACKGROUND & MOTIVATION

- **Ammonia (NH_3) is one of the most important chemical building blocks for manufacture of many chemical commodities and has crucial application as fuel (Figure 1).**

Figure 1: Ammonia applications.

- **The energy uses of NH_3 have always been significant to human life since the past and is claimed to play increasingly important role in the future applications (Figure 2).**

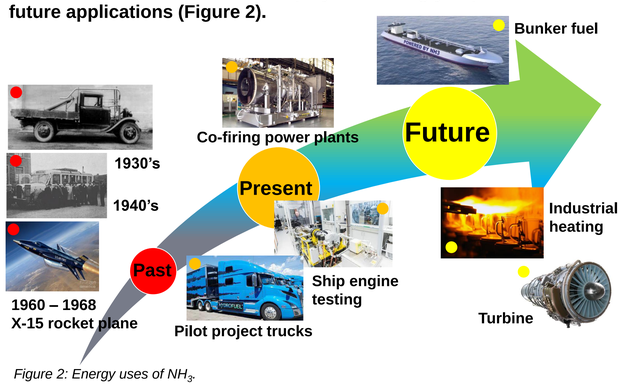

Figure 2: Energy uses of NH_3.

- **However, NH_3 primary production is non-environmentally friendly and energy intensive. As such. we have recently demonstrated the formation of NO_x intermediates via plasma reaction and subsequent electrocatalytic NO_x reduction reactions (NO_xRR) as a potential pathway to generate complete green NH_4^+ ions with high yield (Figure 3).[1-3]**

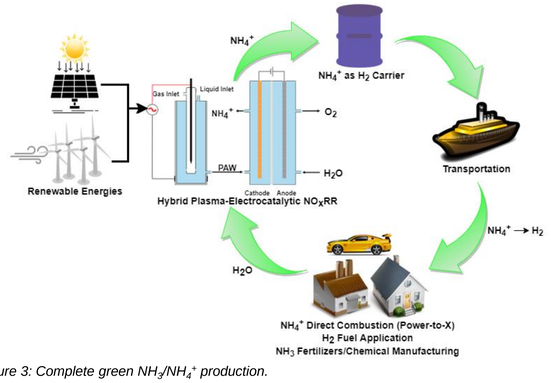

Figure 3: Complete green NH_3/NH_4^+ production.

AIMS

- **To generate simple and inexpensive NO_xRR catalyst to effectively produce high yield NH_4^+ at low applied potential**
- **To determine the correct oxidation state of Cu (CuO, Cu_2O or Cu) as the most effective active sites that favor NO_xRR through surface chemistry tuning of CuO_x/CuF catalysts by electrodeposition**

METHODOLOGY

① CuO_x/CuF synthesis via electrodeposition

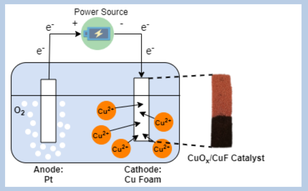

Figure 4: Electrodeposition process.

② NO_xRR-to-NH_4^+

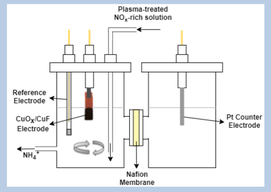

Figure 5: NO_xRR process.

③ NH_4^+ product analysis: Indophenol-blue test

Figure 6: Indophenol-blue test .

④ Catalyst characterisation tests

RESULTS & DISCUSSIONS

CuO_x/CuF Catalyst Characterization Tests

- **Normalized X-ray diffraction (XRD) pattern (Figure 7) reveals that irrespective of the deposition time, Cu {111}, Cu {200}, Cu {220}, Cu_2O {111}, Cu_2O {200}, and Cu_2O {220} are formed on the catalysts**
- **400s sample shows the highest normalized intensity peak for all Cu_2O types, inferring it has the highest amount of Cu_2O**

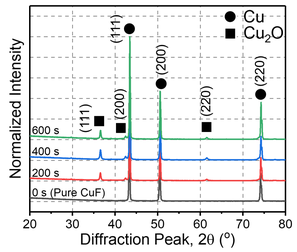

Figure 7: Normalized XRD pattern.

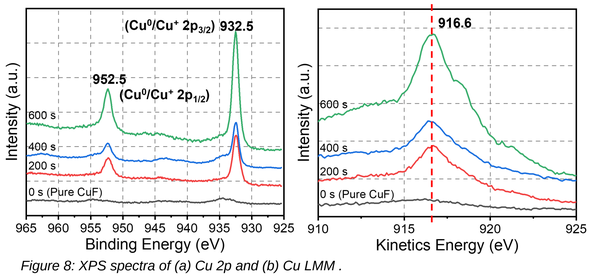

Figure 8: XPS spectra of (a) Cu 2p and (b) Cu LMM .

- **Cu 2p X-ray photoelectron (XPS) measurement (Figure 8a) demonstrates high intensity peak at binding energy of ~ 932.5 and 952.5 eV for all CuO_x/CuF catalysts. This indicates that in addition to metallic Cu, there is also formation of Cu^+**
- **The Auger parameters (i.e., the summation of 932.5 eV binding energy and 916.6 eV kinetics energy from Cu LMM spectra in Figure 8b) for all catalysts is < 1850 eV, signifying that Cu^+ is the main oxidation state on the surfaces**

- **Normalized Raman profile (Figure 9) presents Cu oxide species trend of CuO_x/CuF catalysts with increasing electrodeposition duration as follows:**
  $Cu_2O_x \rightarrow Cu_2O_\delta \rightarrow Cu_2O \rightarrow CuO_{1-x} \rightarrow CuO$ with x<1
- **400s sample shows the highest normalized intensity peak for wavenumber of Cu_2O ($218\ cm^{-1}$), indicating that it has the highest amount of Cu_2O**

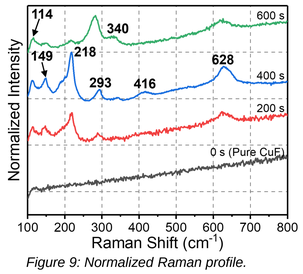

Figure 9: Normalized Raman profile.

NO_x Reduction Reaction to Produce NH_4^+

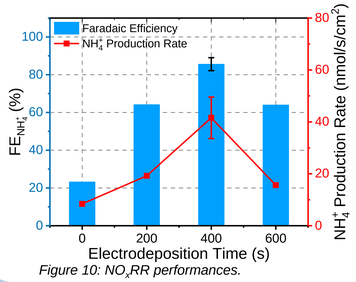

Figure 10: NO_xRR performances.

When tested at -0.5 V_{RHE} (Figure 10), 400s sample achieves:

- **The highest Faradaic efficiency towards NH_4^+ (FE_{NH4^+}) of > 85%**
- **The highest NH_4^+ production rate of ~ 43 nmol/s/cm²**

KEY FINDINGS

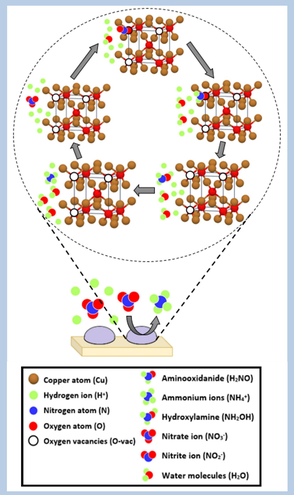

Figure 11: NO_xRR reaction mechanism by Cu_2O.

Complementing characterization results and NO_xRR-to-NH_4^+ production performances, we can deduce that:

- **NH_4^+ production activity from NO_xRR is positively correlated to the Cu_2O amount.**
- **Cu_2O is the most effective active sites for NO_xRR to producing NH_4^+ as compared to metallic Cu and CuO.**
- **Formation of oxygen vacancies in Cu_2O is thermodynamically more favorable as compared to CuO,[4] which in turn, assist with the NO_xRR pathway as illustrated in Figure 11 and the selectivity trends towards NH_4^+**

Comparing CuO_x/CuF catalyst to other state-of-the-art NO_xRR catalysts that also perform under acidic condition (Figure 12), CuO_x/CuF catalyst is more competent than others as it displays higher NH_4^+ yield at lower potential.

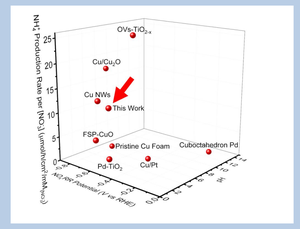

Figure 12: State-of-the-art catalysts for NO_xRR

CONCLUSIONS

In summary, we report:

- **The benefits of Cu_2O species over other Cu species (metallic Cu and CuO) in facilitating the NO_xRR-to-NH_4^+ production**
- **Using electrodeposition method, we are able to tune the surface chemistry of the CuO_x/CuF catalyst. Our NO_xRR measurements reveal that catalyst generated at 400s and -1.0 V_{RHE} is the most optimum of all: NH_4^+ production rate of 43 $nmols^{-1}cm^{-2}$ with a FE_{NH4^+} > 85% at -0.5 V due to having the greatest amount of Cu_2O**
- **The capability of Cu_2O in improving conversion of NO_x into NH_4^+ can be ascribed to the higher amounts of oxygen vacancies naturally present in Cu_2O as compared to CuO and metallic Cu**
- **In brief, our catalyst also displays the economic feasibility and applicability of NO_xRR intermediary approach to generate green NH_3 for P2X and hydrogen economy**

REFERENCES

(1) Sun, J et al. (2021), *EES*, *14* (2).
(2) Daiyan, R et al. (2021), *EES, 14* (6).
(3) Daiyan, R et al. (2020), *ACS Energy Lett., 5* (12).
(4) Davó-Quiñonero, A et al. (2020) *ACS Catal., 10* (11).

ACKNOWLEDGEMENTS

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