BOROCARBONITRIDES: METAL FREE ELECTROCATALYST FOR ELECTROCHEMICAL REDUCTION OF CO$_2$

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Introduction

- Rising atmospheric CO\textsubscript{2} levels has drastic effects on the climate of earth
- Electrochemical reduction of CO\textsubscript{2}(ECO2RR) is an effective approach to reduce atmospheric CO\textsubscript{2} levels and convert CO\textsubscript{2} into value added fuels
- Metals are widely studied but they suffer with drawbacks such as high cost and undesirable competing HER
- Carbon-based materials offer an alternative approach
- Pristine carbon materials are inert towards ECO2RR, doping with heteroatoms such as N can alter the properties which renders carbon active towards ECO2RR
- In this work we study the effect of doping B and N in activated charcoal
Borocarbonitrides: Synthesis and Characterization

- Borocarbonitride synthesized by high temperature reaction of activated charcoal, urea and boric acid
- Composition of B and N in carbon can be altered by changing the amounts of reactant
- BCN exhibit high specific surface area and a high CO₂ uptake in comparison with undoped activated charcoal

Figure 1: (a) Schematic structure of BCN, (b) TEM image

\[ \text{H}_3\text{BO}_3 + \text{CO(NH}_2\text{)}_2 + \text{C} \rightarrow \text{B}_x\text{C}_y\text{N}_z \]

Increasing B,N content

BCN-1
BCN-2
BCN-3
BCN-4

(c) FTIR spectra showing nature of bonds in BCN, (d) Nature of N defects in BCN, (e) N₂-adsorption isotherms
Electrochemical Activity

- Electrochemical activity of BCN was studied in an aqueous bicarbonate electrolyte with continuous CO₂ purging.
- BCN reduces CO₂ to form CO as the only product.
- BCN-3 exhibits highest FE₃CO of 99% at -0.45V in comparison of N-doped carbon which reaches a maximum FE₃CO of 92% at -0.6V.
- BCN is more stable than N-doped carbon.

Figure 2: (a) LSV (b) FE₃CO as a function of potential, (c) constant potential electrolysis and (d) FE₃CO over 24 hours.

Figure 2: TEM image of (e) N-doped carbon and (f) BCN after 24 hours of constant potential electrolysis.
Doped carbons; BCN and NC all exhibit higher CO$_2$ uptake than AC.
- Among BCN, BCN-3 exhibits highest CO$_2$ uptake of 14.5 mmol/g.

- DFT studies suggest that pyridinic N site is most favorable for ECO2RR followed by pyrrolic and graphitic.
- BCN has higher concentration of pyridinic N site compared to NC.

NC has lowest charge-transfer resistance.
- Charge transfer resistance increases with increase BN content due to insulating BN domains.
Conclusion

- N-sites are the active center for ECO2RR in N-doped carbon, but reaching a high doping levels of N is difficult
- Incorporation of Boron with Nitrogen in carbon lattice leads to the formation of borocarbonitrides, where the content of B,N can be tuned and a high doping levels can be achieved
- Borocarbonitrides reduce CO$_2$ to CO in aqueous bicarbonate electrolyte
- Concentration of pyridinic N site is higher in BCN which is responsible for efficient ECO2RR
- BN domains in BCN impart structural stability to the catalyst

References:

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