Boron-doped Electro catalysts Derived from Carbon Dioxide

Jae W. Lee
Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea
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- Recent work: CO$_2$ Conversion to Graphene Oxide
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Previous Research: CO$_2$ to Carbons

At high T and P to carbon materials

- **Porous Carbon**
  - T = 480-500 °C
  - P = 32 MPa
  - Na, Li, K

- **Diamond & Graphite**
  - T = 440 °C
  - P = 80 MPa
  - Na

- **CNT**
  - T = 550 °C
  - P = 70 MPa
  - Li

- **Dry Ice**
  - Mg

- **Graphene**
  - T = 1000 °C
  - P = 100 MPa
  - Mg

- **Fullerene**

- **Porous Carbon**
  - T = 480-500 °C

- **Graphene**
  - T = 1000 °C

- **Fullerene**
  - T = 440 °C

- **Diamond & Graphite**
  - T = 440 °C

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Chakrabarti et al., J. Mat. Chem., 2011
CO$_2$ to Carbon Energy Materials


+ NaBH$_4$
500 °C & 1 bar

BN-GO

100 °C & 30 bars/
700 °C & 1 bar

B-PC

Supercapacitor
Zhang & Lee, ACS SCE, 2014

Fuel cell ORR catalyst
Byeon & Lee, JPCC, 2013
Zhang et al., JMCA, 2013
Zhang & Lee, Carbon, 2013
Zhang et al., JPCC, 2012.
Chemistry World, Jan., 2012.

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CO₂ Conversion to Graphene Oxide At Mild Conditions

1. Carbon fixation (T < 100°C, P < 3MPa)
   - OCH₃, HCOO, aliphatic groups

2. Graphenization (600-750°C, 0.1MPa of N₂)
   - Pyrolysis
   - G.O-boron oxide nanocomposites

Chemistry World, Jan., 2012.

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Significance

- Formation of aliphatic groups from CO\(_2\) (Organic Synthesis)
- Novel route for reducing CO\(_2\) efficiently

CO\(_2\)

- Stable in nature
- Hard to employ CO\(_2\) as a raw mat.
- Being amphosteric in nature

NH\(_3\)BH\(_3\)

Problem: GO yield is too low (2-3 wt.% based on starting NH\(_3\)BH\(_3\))
CO₂ to B-doped Porous Carbons

Supercritical CO₂ → Porous carbon (J. Am. Ceram. Soc., 2011, 94, 3078)

CO₂ at atmospheric P → Porous carbon (not reported)

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CO$_2$ + NaBH$_4$ Reaction

- Thermal analysis of CO$_2$ transformation

- Small-Scale CO$_2$ transformation
Heat flow from TGA

One exothermic peak

Carbon fixation is occurred

- Mass increase by 53%
- Much lower than decomposition T of NaBH₄ (~534 °C)
- 247.5 °C
Heat of Reaction

- Mainly due to \( \text{CO}_2 \) reaction with \( \text{NaBH}_4 \)
- Reaction heat released can increase to the decomposition temp. of \( \text{NaBH}_4 \)

\[ \Delta H = -273 \text{ KJ/mol} \]
CO₂ Conversion at Different T

<200°C>

<300°C>

<400°C>

insignificant exothermic peak

insignificant weight increase

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CO₂ + NaBH₄ at 500°C
ATR-FTIR (200°C)

- B-O stretching
- B-H deformation
- OCO stretching (COOH)
- B-H stretching

$\rightarrow$ NaBH$_4$ remains

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ATR-FTIR(300°C)

- Structural feature of NaBH₄ disappear
- Appearance of new bands
- Presence of OCH₃
ATR-FTIR(400°C, 500°C)

- C-H rocking (2855 cm⁻¹)
- C-H stretching (2920 cm⁻¹)

No formate groups
- Partially decomposed product
Summary (ATR-FTIR)

- $T$ increases
- Transform increases
- CH$_3$ rocking band increases

200°C: CO$_2$ transformation is slow
XRD Results: Two by-products

NaBO(OCH₃)(O₂CH) → NaBO₂ + HCO₂CH₃

Reduction of CO₂ with Na(1ˢᵗ decomposition product of NaBH₄)

Salts leached out after washing

two main crystalline products
Treatment of B-PC: Washing Salts

- **Treatment**

  - \(\text{CO}_2^+ + \text{NaBH}_4\)
  - \(500^\circ\text{C}\) at 1 Bar
  - 5 M HCl washing or Hot water washing
  - Drying
  - B-PC

- **Characterization of B-PC**

  - Micro-Raman, \(^{13}\text{C}\) MAS-NMR, SEM, BET

  *After washing, B-PC yield: 15-20 wt% of NaBH}_4*
After treatment, the BET surface area increased from 1.5 to 342 m²/g.

Consistent

Treated solid → Porous

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Raman spectra & NMR

D, G band – breathing & stretching mode of sp² bonded carbon

Structural feature of solid carbon

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XPS (X-ray photoelectron spectroscopy)

189 eV: BC$_3$
192.5 eV: BCO$_2$

Confirms boron insertion!!
CO$_2$ → B-PC at 1 bar, Great!!

- Solid carbon is produced from reaction
- Treated solid is porous carbon

What’s next?

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Boron-Doped → ORR in Fuel Cell Cathode

**Electrochemical measurements:**
CV (cyclic voltammetry) & RDEV

**Activation of BPC - NaBH₄ treatment**
(Zhang et al., JMCA, 2013)

**Chemical reaction:**

\[ \text{CO}_2 + \text{NaBH}_4 \rightarrow 500 \, ^\circ\text{C} \text{ at 1 bar} \]
ORR Performance of B-PCs (CV)

Current density (A/cm²)

E vs. Ag/AgCl (V)

-0.21 V
-0.31 V
ORR Performance of B-PCs (RDEV)

**Graphical Description:**
- **Axes:**
  - X-axis: E vs. Ag/AgCl (V)
  - Y-axis: Current density (A/cm²)
- **Lines:**
  - Pink line: Pt-AC
  - Red line: PB-PC
  - Blue line: TB-PC
- **Key Points:**
  - -0.1 V
  - -0.15 V
  - -0.04 V
  - 2500 rpm at a scan rate of 10 mV s⁻¹

**Textual Information:**
- 0.04 V - 0.15 V
- Pt-AC, PB-PC, TB-PC
- Current density vs. E vs. Ag/AgCl

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XPS: Surface Composition Change from B-C to B-C-O after NaBH₄ Treatment

187.8 eV: B₄C

191.4 eV: BCO₂

Binding Energy (eV)
TEM & XRD of PB-PC and TB-PC

Broad diffraction peak centered at ca. 23.5°
Amorphous Carbon!!
SEM and Raman of PB-PC and TB-PC

SEM: more ordered

$I_D/I_G$ (the ratio of peak heights): 0.66 and 0.93 for PB-PC and TB-PC.  $E_g \downarrow$

$$\frac{I_D}{I_G} = C' (\lambda) L_a^2 = \frac{C''}{E_g^2}$$

Ferrari and Robertson (2000)
Methanol Tolerance Test

Chronoamperometric responses to methanol introduction

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Durability Test: CV 5000 Cycles

Current (A) vs. Potential vs. Ag/AgCl (V)

ORR durability test in O₂ saturated 1.0 M NaOH

-0.21 → -0.25 V

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BPC to Supercapacitors

Activation of BPC
- KOH treatment
- CO₂ treatment

Electrochemical measurements:
Cyclic voltammetry (CV) & Galvanostatic

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Zhang & Lee, ACS SCE, 2014
Cyclovoltammetry (CV)

Potential (V vs. Ag/AgCl) vs. Current (A/g)

K-BPC
MC
U-BPC

Zhang & Lee, ACS SCE, 2014
Specific Capacitance

Galvanostatic measurements

Voltage (V) vs. Time (s)

-0.4 to 0.6

-0.4 to 0.6

Current density (A/g)

1.35 A/g

2.7 A/g

4.05 A/g

6.76 A/g

130 – 135 F/g

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Zhang & Lee, ACS SCE, 2014
Durability Test (3500 cycles)

Cycle number

Capacitance (F/g)

130 – 135 F/g

Zhang & Lee, ACS SCE, 2014
Feasible Green Process

Carbon negative

Solar Energy

\[ \text{CO}_2 + \text{NaBH}_4 \rightarrow 500^\circ\text{C} \]

발열: -273 KJ/mol

Supercapacitor

Fuel cell ORR catalyst

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Future Directions

- Economical CO$_2$ Conversion – Green Processes
- Fuel Cell Electrode: Replacing Pt catalysts: BPC + Metal(s)
- Supercapacitors: EDLC, Pseudo-capacitors, & Hybrid capacitors
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