Hetero-atom Substituted Carbon Alloys for Energy Conversion and Storage

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Osaka Electro-Communication University
Japan
In Osaka

Osaka Castle

Umeda Sky Building

Famous signboard of crab restaurant
Apparatus in my lab

CVD apparatus

HFCVD apparatus

Photo catalytic measurement
Today’s talk

1. Energy storage system in near future
2. Hetero-atom substitute carbon alloys: B/C/N materials
   2-1. Intercalation of 1st and 2nd group metals into B/C/N materials
   2-2. Intercalation mechanism
   2-3. Application of intercalation to Na ion secondary batteries
3. Hetero-atom substitute carbon alloys: C/N materials
   3-1. Application of C/N materials to capacitors
   3-2. Application of C/N materials to catalyst for electrolysis of water
Energy storage system in near future
Natural resources for energy production
Ex: Solar cell

- Solar Cell
- Direct current
- Highly efficient
- At home
- Storage to secondary batteries
- Transform to alternating current
- Power company

Ex: Solar cell
- Day
- Highly efficient
- Storage to secondary batteries

Nissan LEAF
Secondary batteries in the next generation

Natural resources
Clarke number
Ca > Na > K > Mg > Ba > Li
3.4  2.6  2.4  1.9  0.006

Anode materials for Li-ion batteries has been increasing.

Next generation?
Ca, Na, Mg ion batteries

Good host materials?
Hetero-atom substitute carbon alloys: B/C/N materials
What is Carbon Alloy?

New host materials

Hetero-atom substituted carbon alloys

B/C materials  \( \text{BC}_3 \)  
C/N materials  \( \text{C}_2\text{N}, \text{C}_3\text{N}, \text{C}_5\text{N} \)  
B/C/N materials  \( \text{BCN}, \text{BC}_2\text{N}, \text{BC}_3\text{N}, \text{BC}_4\text{N}, \text{BC}_6\text{N} \)  

\[ \text{BC}_2\text{N}-\text{Type}\text{B} \quad (\text{B}_{24}\text{C}_{48}\text{N}_{24}) \]
Preparation methods for B/C/N materials

**CVD method** $\rightarrow$ $\text{BC}_2\text{N}^*$, $\text{BC}_3\text{N}^{**}$, $\text{BCN}^{**}$, $\text{BC}_6\text{N}^{***}$


**Solid-gas reaction** $\rightarrow$ $\text{B/C/N}^*$, $\text{BC}_3\text{N}^{**}$


**Precursor pyrolysis method** $\rightarrow$ $\text{BC}_4\text{N}^*$, $\text{B/C/N}^{**}$


CVD apparatus for preparation of B/C/N materials

\[ 2\text{CH}_2\text{CHCN} + \text{BCl}_3 \rightarrow \text{BC}_6\text{N} + 3\text{HCl} + \text{NH}_3 \]


**Preparation condition**

- **Gas flow rate**
  - \( \text{CH}_2\text{CHCN} \) (Acrylonitrile): 40ml/min
  - \( \text{BCl}_3 \) (Boron trichloride): 20ml/min
- **Reaction time**: 120min
- **Temperature**: 1470K ~ 2070K
- **Pressure**: 760mmHg
X-ray powder diffraction patterns for BC$_6$N.

Graphite: mesocarbon microbeads heat-treated at 3230K
Intercalation of 1st and 2nd group metals into B/C/N materials
### Intercalation of group 1 and 2 metals into B/C/N materials

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ion diameter</strong></td>
<td>180 pm⁺</td>
<td>232 pm⁺</td>
<td>304 pm⁺</td>
<td>172 pm⁺</td>
<td>228 pm⁺</td>
</tr>
<tr>
<td><strong>BC₂N</strong></td>
<td>1st stage*¹,²</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>$d_i = 370$ pm</td>
<td></td>
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<tr>
<td></td>
<td>1st stage*²</td>
<td></td>
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<tr>
<td></td>
<td>$d_i = 430$ pm</td>
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<td></td>
<td>1st stage*¹,²</td>
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<tr>
<td></td>
<td>$d_i = 542$ pm</td>
<td></td>
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</tr>
<tr>
<td><strong>BC₆N</strong></td>
<td>1st stage*³</td>
<td></td>
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<tr>
<td></td>
<td>$d_i = 365$ pm</td>
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<tr>
<td><strong>Graphite</strong></td>
<td>1st stage</td>
<td></td>
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<tr>
<td></td>
<td>$d_i = 370$ pm</td>
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<tr>
<td></td>
<td>8th stage</td>
<td></td>
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<tr>
<td></td>
<td>$d_i = 460$ pm</td>
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<tr>
<td></td>
<td>1st stage</td>
<td></td>
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<tr>
<td></td>
<td>$d_i = 541$ pm</td>
<td></td>
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<tr>
<td></td>
<td>No intercalation</td>
<td></td>
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<tr>
<td><strong>Intercalation</strong></td>
<td>Already used for the Li ion batteries</td>
<td></td>
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<tr>
<td><strong>Under investigation</strong></td>
<td>Under investigation for the Na ion batteries</td>
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<tr>
<td><strong>Hopefully</strong></td>
<td>Hopefully Mg and Ca ion batteries in the future</td>
<td></td>
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</tbody>
</table>
Galvanostatic charge/discharge curves of the BC₆N prepared at 1470K in 1M-LiPF₆/EC+DEC. Current density: 100μA/cm².

1st stage Li-intercalated compound

GIC: \( \text{Li}_x\text{C}_6 \)

\( \text{Li}_x\text{BC}_6\text{N} \)
Preparation of $\text{BC}_2\text{N}$ by CVD method

\[ \text{CH}_3\text{CN} + \text{BCl}_3 \rightarrow \text{BC}_2\text{N} + 3\text{HCl} \]


**Preparation condition**

- **Gas flow rate**
  - CH$_3$CN (Acetonitrile) $\quad$ 40 ml/min
  - BCl$_3$ (Boron trichloride) $\quad$ 40 ml/min

- **Reaction time**
  - 120 min

- **Temperature**
  - 1470 K $\sim$ 2070 K

- **Pressure**
  - 760 mmHg
Intercalation of alkali metal into BC$_2$N

**Two bulb method**

Before the intercalation

After the intercalation
Ex: 620 K for Na intercalation
Na-BC$_2$N prepared by vapor phase reaction

X-ray diffraction pattern of Na-intercalated BC$_2$N (Reaction temp.: 620K. Host BC$_2$N was prepared at 2070K.)

- Host BC$_2$N was prepared at 2070K.
- Na-GIC(8th stage)
  - Intercalated layer = 450 pm
- Interaction Na-BC$_2$N > Na-GIC

$d = 430$ pm
(1st: 001)

$d = 215$ pm
(1st: 002)

Intercalation of Mg into BC$_2$N

Stainless steel tube and cap

Setting in a glove box under Ar atmosphere

Heat-treatment in a furnace at 920K

m.p. of Mg = 920K
Mg-BC$_2$N prepared by vapor phase reaction

X-ray diffraction pattern of Mg-intercalated BC$_2$N. Host BC$_2$N was prepared at 2070K.
Intercalation mechanism
X-ray absorption (XAS) and emission spectroscopy (XES)

Unoccupied orbitals
occupied orbitals
Inner orbitals

XAS XES

Band gap

E

hv

hv'

Photo current

Total electron yield (TEY)

(Advanced Light Sources in LBL, California)
TEY X-ray absorption spectrum in the CK region of BC$_2$N film, compared with those of graphite, non-crystalline carbon and BC$_6$N. Incident angle: 45°.
TEY X-ray absorption spectrum in the CK region of BC$_2$N film, compared with those of graphite, non-crystalline carbon and BC$_6$N. Incident angle: $45^\circ$. 
Ionization potentials of metals and electron affinities of host materials

Born-Haber Cycle

\[ \Delta H_f = S + \frac{1}{2}D + IE - EA + U \]

- \( \Delta H_f \): Formation Enthalpy
- \( S \): Heats of Sublimation
- \( D \): Dissociation Energy
- \( IE \): Ionization Potential
- \( EA \): Electron Affinity
- \( U \): Lattice Energy

\[ U = - \frac{N_A M z + z - e^2}{4 \pi \varepsilon_0 r_0} \left(1 - \frac{1}{n}\right) \]
Application of intercalation to Na ion secondary batteries
Electrochemical intercalation of Na into BC$_2$N

Discharge/charge curves of Na$_x$BC$_2$N by galvanostatic method in 1M-NaPF$_6$/EC+DEC. Current density: 100 $\mu$A/cm$^2$. WE: BC$_2$N prepared at 1770K.
Na-BC$_2$N powder prepared by CCCV method

Na-BC$_2$N (0.7V vs. Na/Na$^+$) by CCCV method in NaPF$_6$/EC+DEC. WE: BC$_2$N prepared at 1770K.
Na-BC$_2$N film prepared by CCCV method

Na-BC$_2$N (full discharge: 0.003V vs. Na/Na$^+$ in NaPF$_6$/EC+DEC. WE: BC$_2$N prepared at 1770K.)
Carbon Alloy (CA) ORR Catalysts (CAOC)

Discovered and named by the Gunma Univ. Carbon Laboratory

**Introduction of**

- Heteroatoms
- Structural defects
- Porosity

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**Two types of CAs by GUCL**

- **Nanoshell structure**
  - Surface defects are important
  - 20–50 nm

- **BN-doping**
  - B-N-C moiety is important

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**Costdown**

- sp² dominant carbons

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Hetero-atom substitute carbon alloys: C/N materials
Preparation methods for C/N materials

**CVD method** $\rightarrow$ $C_xN^*$, $C_3N_4$ type**

* T. Nakajima et al., Carbon 35 (1997) 203.
** M. Kawaguchi et al., Carbon 42 (2004) 345.

**Solid-gas reaction** $\rightarrow$ $(C_3N_3)_2(NH)_3^*$, $C_3N_4$ type**


**Precursor pyrolysis method** $\rightarrow$ $C_xN^*$, $C_3N^{**}$, $C_2N^{***}$

* H. Konno et al., Carbon 35 (1997) 669.
** M. Kawaguchi et al., J. Power Sources 172 (2007) 481.

**Template method** $\rightarrow$ $C_xN$

C/N materials prepared by the present authors

Layered material

Yellow

2C₃N₃Cl₃ + 3NH₃ → (C₃N₃)₂(NH)₃ + 6HCl


C₃N₄ type: sp³ hybridized

C₃N₃Cl₃ + Li₃N → C₃N₄ + 3LiCl


White

CVD

3CCl₄ + 16NH₃ → C₃N₄ + 12NH₄Cl


Layered material

Black

C₁₀N₈ → C₆N₄ (+ 2C₂N₂) → C₃N


Photoluminescence

Host material

Hardness

Photoluminescence

Electrochemical capacitor

Photo catalyst
Color of C/N materials

- $\text{C}_3\text{N}_4$ type
- $(\text{C}_3\text{N}_3)_2(\text{NH})_3$
- $\text{C}_2\text{N}$
Application of C/N materials to capacitors
Preparation and application of C/N materials

CAN: 2,3,6,7-tetracyano 1,4,5,8-tetraazanaphthalene

Composition: $\text{C}_3\text{N}$

Application

HT at 1070K

HT at 1020K

AMN: diaminomaleonitrile

Composition: $\text{C}_2\text{N}$

Capacitors

Adsorbents

Photo catalysts
Structure of C/N material

XRD patterns of C/N materials prepared by the pyrolysis of AMN at the temperature between 470K and 1270K.
Compositions of C/N materials prepared by the pyrolysis of AMN at various temperatures.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMN1120K</td>
<td>4.0</td>
<td>1.3</td>
</tr>
<tr>
<td>AMN1070K</td>
<td>4.0</td>
<td>1.7</td>
</tr>
<tr>
<td>AMN1020K</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>AMN</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

FTIR spectra of C/N material
Chemical bonds in C/N material

ESCA N1s spectra of C/N materials prepared from AMN at (A) 970K, (B) 1020K, (C) 1070K, (D) 1120K, and (E) 1170K.
C/N material prepared from AMN

Heat-treatment at 1020K $\to$ Composition: $\text{C}_2\text{N}$

Comparison of CV curves

Figure  Cyclic voltammograms for (a) C/N material prepared by the pyrolysis of AMN at 1020K (BET:230 m²/g) and (b) activated carbon (BET:2300 m²/g). 1M-H₂SO₄ aqueous solution. Scan speed:1mV/sec. Three electrode cell.

Comparison of capacitive performances

<table>
<thead>
<tr>
<th></th>
<th>AC</th>
<th>C$_3$N</th>
<th>C$_2$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity (F/g)</td>
<td>180</td>
<td>160</td>
<td>200</td>
</tr>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>2300</td>
<td>880</td>
<td>230</td>
</tr>
<tr>
<td>Capacity per unit surface area (F/m$^2$)</td>
<td>7.83 × 10$^{-2}$</td>
<td>18.2 × 10$^{-2}$</td>
<td>91.3 × 10$^{-2}$</td>
</tr>
<tr>
<td>Apparent density (g/cm$^3$)</td>
<td>0.34</td>
<td>0.68</td>
<td>0.65</td>
</tr>
<tr>
<td>Volumetric capacity (F/cm$^3$)</td>
<td>61</td>
<td>110</td>
<td>130</td>
</tr>
</tbody>
</table>

AC: activated carbon  
CAN1070K: C/N material prepared from CAN (2,3,6,7-tetracyano 1,4,5,8-tetraazanaphthalene)  
AMN1020K: C/N material prepared from AMN (diaminomaleonitrile)
**Water adsorption**

Another important role of nitrogen is C-N → material ↔ water, which increases hydrophilicity.

Figure: Water adsorption isotherm (290K) of C/N material prepared by the pyrolysis of AMN at 1020K, compared with that of activated carbon.
Role of nitrogen in C/N material

1) Increase in hydrophilicity by introduction of nitrogen

\[
\begin{align*}
\text{N:} + \text{H}^+ &\rightarrow \text{N:} + \text{H}^+ \\
\end{align*}
\]

\[\rightarrow \text{Supply of ions into micro pores}\]

and

2) Interaction of pyridine-type nitrogen with protons

\[
\begin{align*}
\text{N:} + \text{H}^+ &\rightarrow \text{N:} + \text{H}^+ \\
\end{align*}
\]

Addition of pseudo capacitance

Application of C/N materials to catalyst for electrolysis of water
Photo catalysts for H$_2$ production from water

  - A lot of researches

  - Not so many researches
  3 wt % Pt was deposited on C$_3$N$_4$ for the supporting catalyst.
Apparatus for measurement of photo catalytic behavior

1.20 V* < 1.23 V vs. SHE

Salt bridge

*1.00 V vs. Ag/AgCl

Visible or UV+Visible Light

0.5M-H$_2$SO$_4$
Photo Catalytic behavior of C$_2$N

Change in photocurrent for C$_2$N prepared from AMN in 1.0 M H$_2$SO$_4$. The electrode was intermittently irradiated by visible light.
Photo Catalytic behavior of C₃N

Change in photocurrent for C₃N prepared from CAN in 1.0 M H₂SO₄. The electrode was intermittently irradiated by visible light.
Comparison of photo catalytic current

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photo current density μA/cm²</th>
<th>Visible light</th>
<th>UV-Visible light</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (1200K)*</td>
<td>1.00</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ (870K)**</td>
<td>$4.50 \times 10^{-1}$</td>
<td>$2.73 \times 10^{2}$</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ (ST-01: powder)</td>
<td>1.35</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>C$_2$N (AMN1020K)</td>
<td>9.87</td>
<td>1.33 \times 10</td>
<td></td>
</tr>
<tr>
<td>(AMN470K)</td>
<td>2.36</td>
<td>2.10</td>
<td></td>
</tr>
<tr>
<td>C$_3$N (CAN1070K)</td>
<td>$1.28 \times 10$</td>
<td>1.55 \times 10</td>
<td></td>
</tr>
<tr>
<td>(CAN670K)</td>
<td>1.47</td>
<td>5.26</td>
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</tr>
</tbody>
</table>

*TiO$_2$ prepared on Ti plate at 1200 K
**TiO$_2$ prepared on Ti plate at 870 K
Photo catalytic behavior of C$_3$N

The electrode was intermittently irradiated by UV with visible light.

Change in open circuit potential for C$_3$N prepared from CAN in 1.0 M H$_2$SO$_4$. The electrode was intermittently irradiated by UV with visible light.
Electronic structure of C₃N in H₂SO₄ aqueous solution
Electronic structure of C$_3$N in H$_2$SO$_4$ aqueous solution
Summary

1. B/C/N materials intercalate Na and Mg to make intercalation compounds, which can be applied to anodes of Na (and Mg in future) ion batteries.

2. C/N materials have several kinds of nitrogen in the structure and adsorb ions on the structure, which can be applied to capacitors and photo catalysts.
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Danke schön!

ご清聴ありがとうございました！