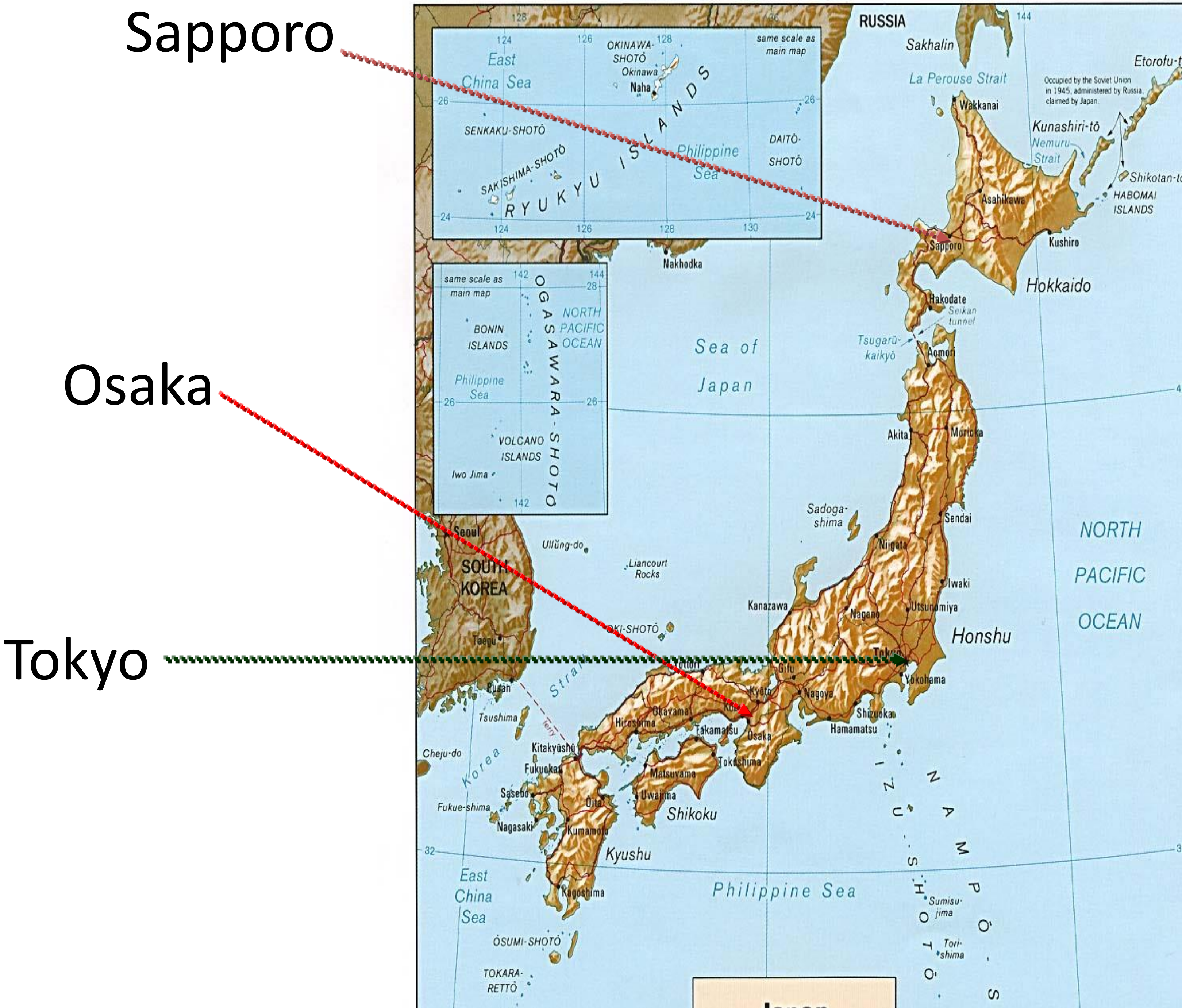
4th German-Japanese Joint Symposium
Sapporo, July 7-8, 2014

Hetero-atom Substituted Carbon Alloys for Energy Conversion and Storage

Masayuki Kawaguchi
Osaka Electro-Communication University
Japan



Sapporo
Osaka
Tokyo
RUSSIA
Sakhalin
La Perouse Strait
Etorofu-tō
Occupied by the Soviet Union in 1945, administered by Russia, claimed by Japan.
Kunashiri-tō
Nemuro Strait
Shikotan-tō
HABOMAI ISLANDS
Wakkanai
Asahikawa
Sapporo
Kushiro
Hokkaido
Hakodate
Seikan tunnel
Tsugarū-kaikyō
Aomori
Akita
Morioka
Sendai
Niigata
Sadoga-shima
Iwaki
Utsunomiya
Nagano
Kanazawa
Honshu
Tokyo
Yokohama
Nagoya
Gifu
Kyoto
Osaka
Kobe
Shizuoka
Hamamatsu
Okayama
Hiroshima
Takamatsu
Tokushima
Matsuyama
Uwajima
Shikoku
Kitakyūshū
Fukuoka
Sasebo
Nagasaki
Ōita
Kumamoto
Kyushu
Kagoshima
Tottori
Nakhodka
Sea of Japan
NORTH PACIFIC OCEAN
Philippine Sea
East China Sea
Seoul
SOUTH KOREA
Taegu
Pusan
Ullŭng-do
Liancourt Rocks
OKI-SHOTŌ
Tsushima
Cheju-do
Korea Strait
Fukue-shima
ŌSUMI-SHOTŌ
TOKARA-RETTŌ
IZU-SHOTŌ
NAMPŌ-SHOTŌ
Sumisu-jima
Tori-shima
East China Sea
OKINAWA-SHOTŌ
Okinawa
Naha
SENKAKU-SHOTŌ
SAKISHIMA-SHOTŌ
RYUKYU ISLANDS
Philippine Sea
DAITŌ-SHOTŌ
same scale as main map
BONIN ISLANDS
OGASAWARA-SHOTŌ
NORTH PACIFIC OCEAN
Philippine Sea
VOLCANO ISLANDS
Iwo Jima

In Osaka

Umeda Sky Building

Osaka Castle

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

Power company

Transform to alternating current

Solar Cell

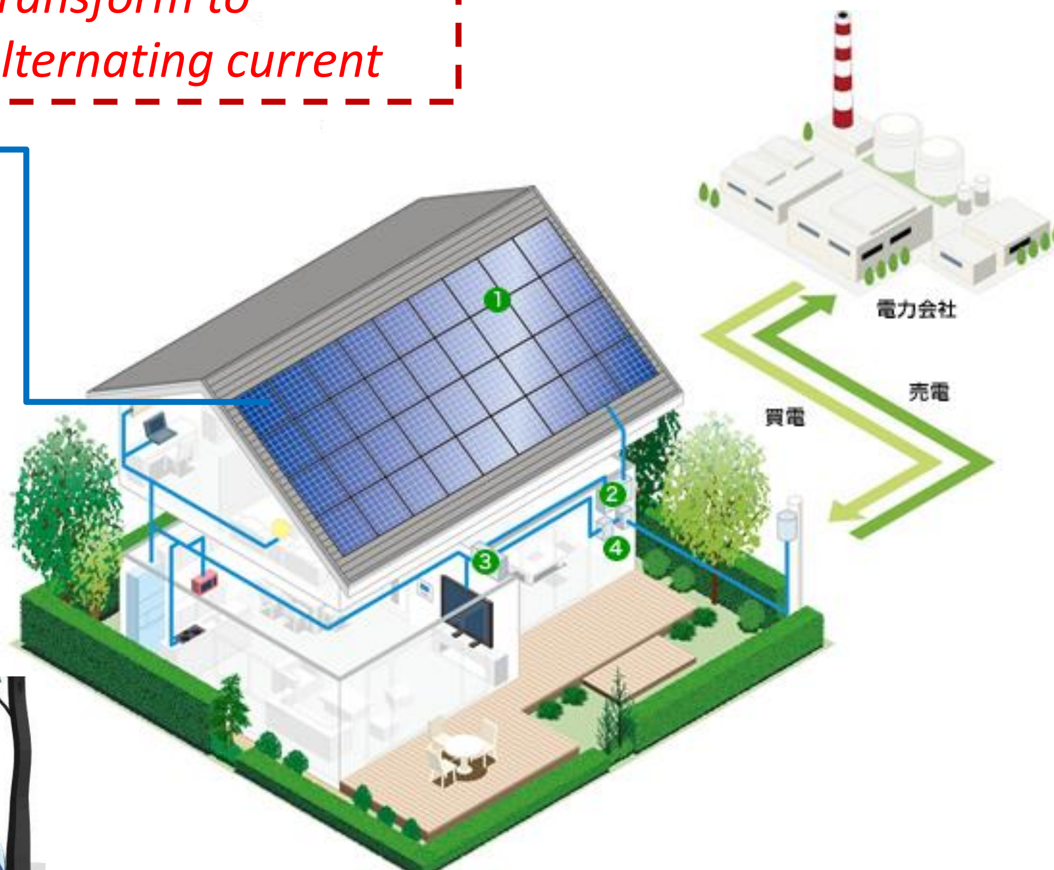
Direct current

Highly efficient

At home

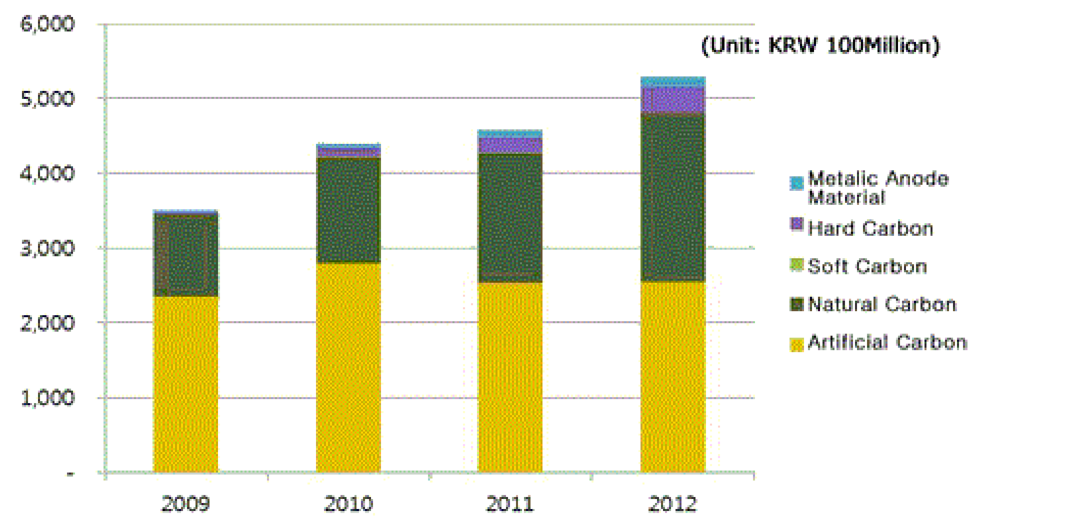
Day

Storage to secondary batteries



Nissan LEAF

Secondary batteries in the next generation



source: Anode Material for Li-ion secondary cell - Technology Trend and Market Forecast Solar&Energy, March, 2012

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.

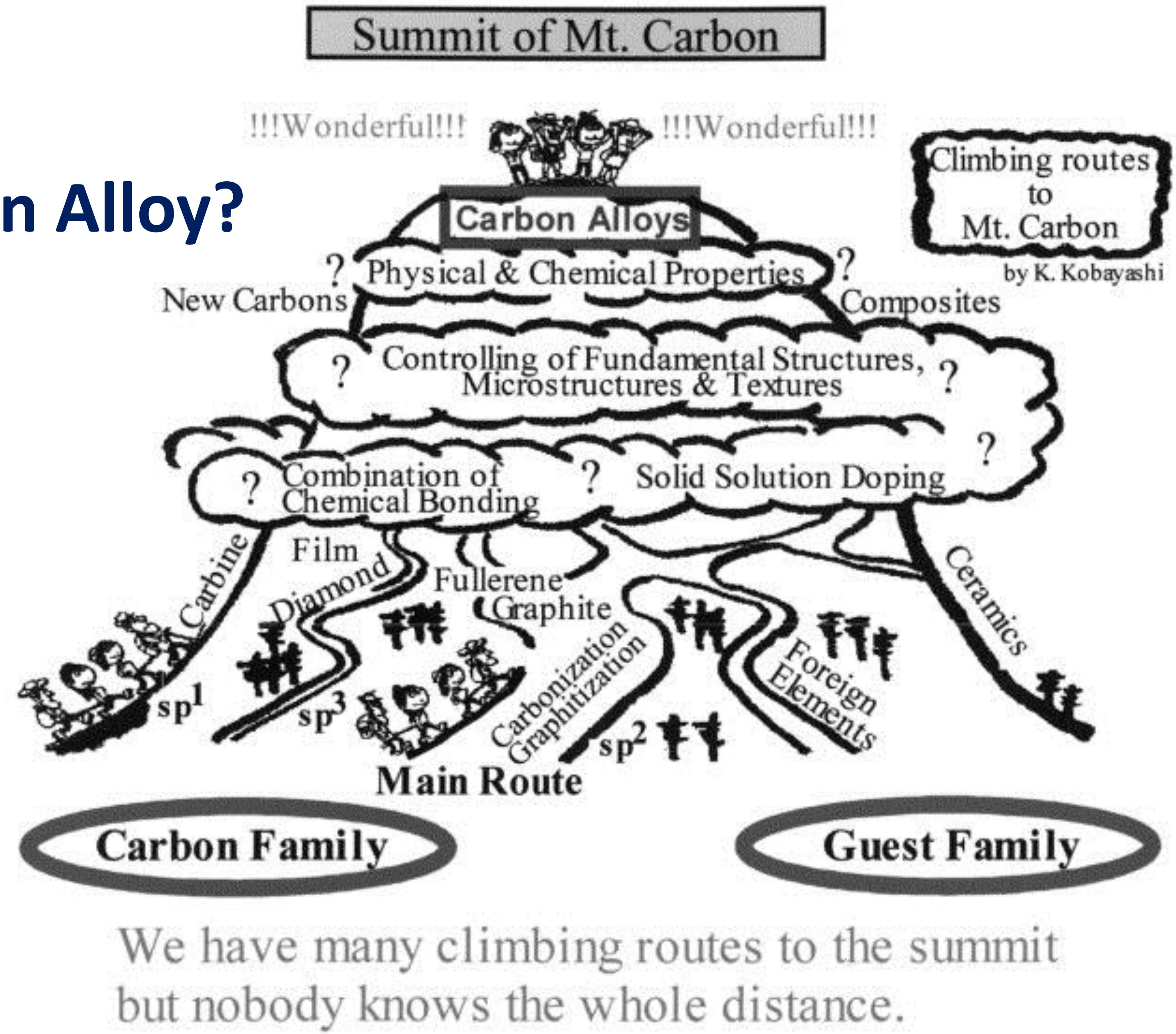
Next generation?

Ca, Na, Mg ion batteries

Good host materials?

Hetero-atom substitute carbon alloys: B/C/N materials

What is Carbon Alloy?



Ref: Y. Tanabe, E. Yasuda, Carbon 38 (2000) 329-334.
E. Yasuda, M. Inagaki, K. Kaneko, M. Endo, A. Oya and Y. Tanabe, *Carbon Alloy* (2003) Elsevier.

New host materials

Hetero-atom substituted carbon alloys

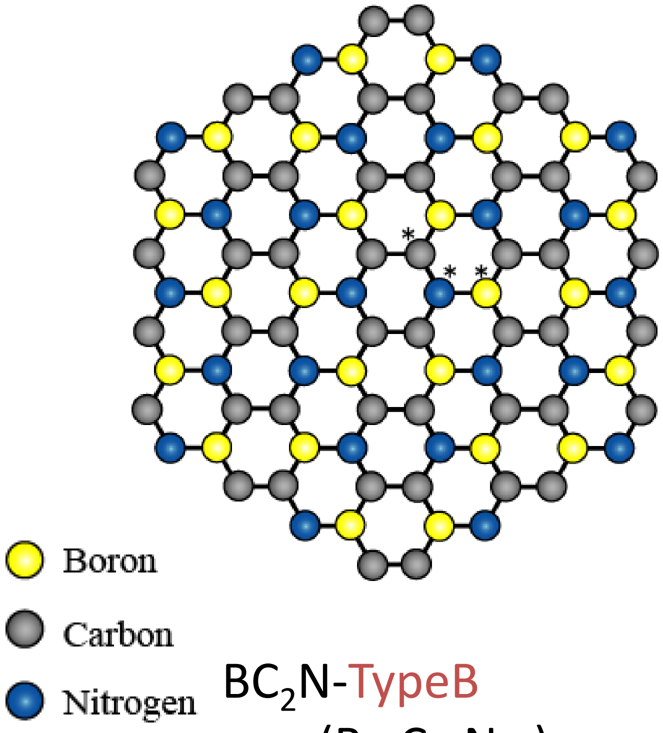
B/C materials BC_3 ・・・

C/N materials C_2N, C_3N, C_5N ・・・

B/C/N materials BCN, BC_2N, BC_3N, BC_4N, BC_6N ・・・

・

・



BC_2N-TypeB

($B_{24}C_{48}N_{24}$)

Preparation methods for B/C/N materials

CVD method → BC_2N^{*}, BC_3N^{**}, BCN^{**}, BC_6N^{***}

*: J. Kouvetakis *et al.*, *Synth. Met.* 34 (1989) 1.

**: M. Kawaguchi et al., *Chem.Mater.*, 8 (1996) 1197.

***: M. Kawaguchi et al., *Carbon*, 37 (1999) 147.

Solid-gas reaction → $B/C/N^{*}$, BC_3N^{**}

*T. Ya. Kosolapova *et al.*, *Pooshkovaya Metallurgiya*, 1 (1971) 27.

**M. Kawaguchi *et al.*, *J.Chem.Soc.,Chem.Commun.*, (1993) 1133.

Precursor pyrolysis method → BC_4N^{*}, $B/C/N^{**}$

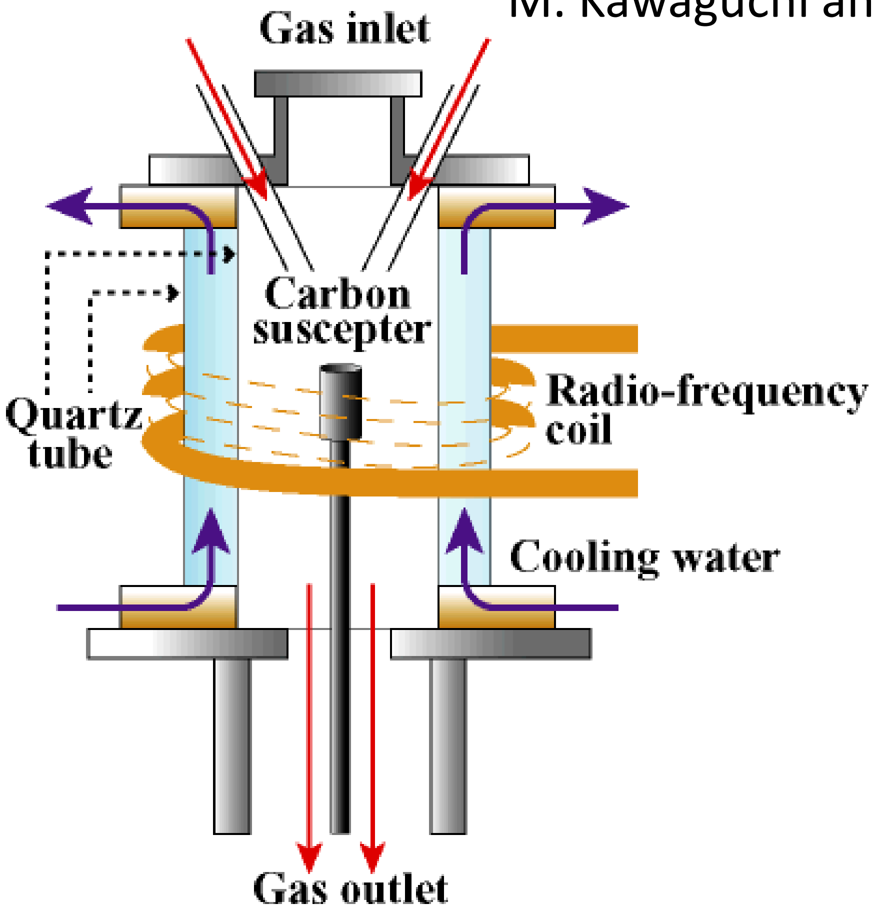
*J. Bill *et al.*, *Eur. J. Solid State Inorg. Chem.* 29 (1992) 195-212.

**H. Konno *et al.*, *J. Power Sources* 195 (2010) 1739.

CVD apparatus for preparation of B/C/N materials

$$2CH_2CHCN + BCl_3 \rightarrow BC_6N + 3HCl + NH_3$$

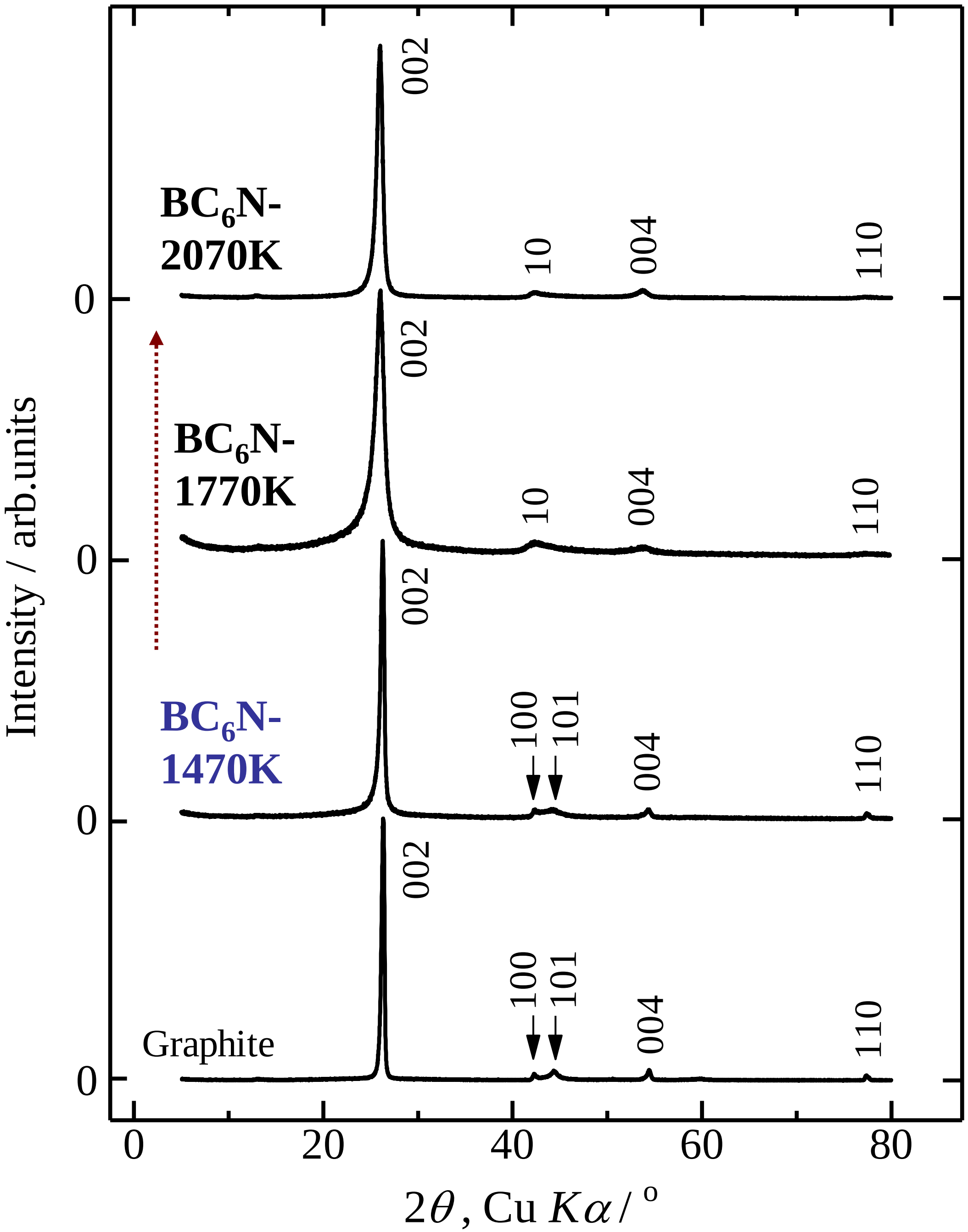
M. Kawaguchi and Y. Wakukawa, *Carbon* **37** (1999) 147-149.



Preparation condition

- Gas flow rate
  - CH_2CHCN (Acrylonitrile)
    - 40ml/min
  - BCl_3 (Boron trichloride)
    - 20ml/min
- Reaction time
  - 120min
- Temperature
  - 1470K ~ 2070K
- Pressure
  - 760mmHg

X-ray powder diffraction patterns for BC_6N.



Highest crystallinity

Thermodynamic reason

Graphite: mesocarbon microbeads heat-treated at 3230K

Intercalation of 1st and 2nd group metals into B/C/N materials

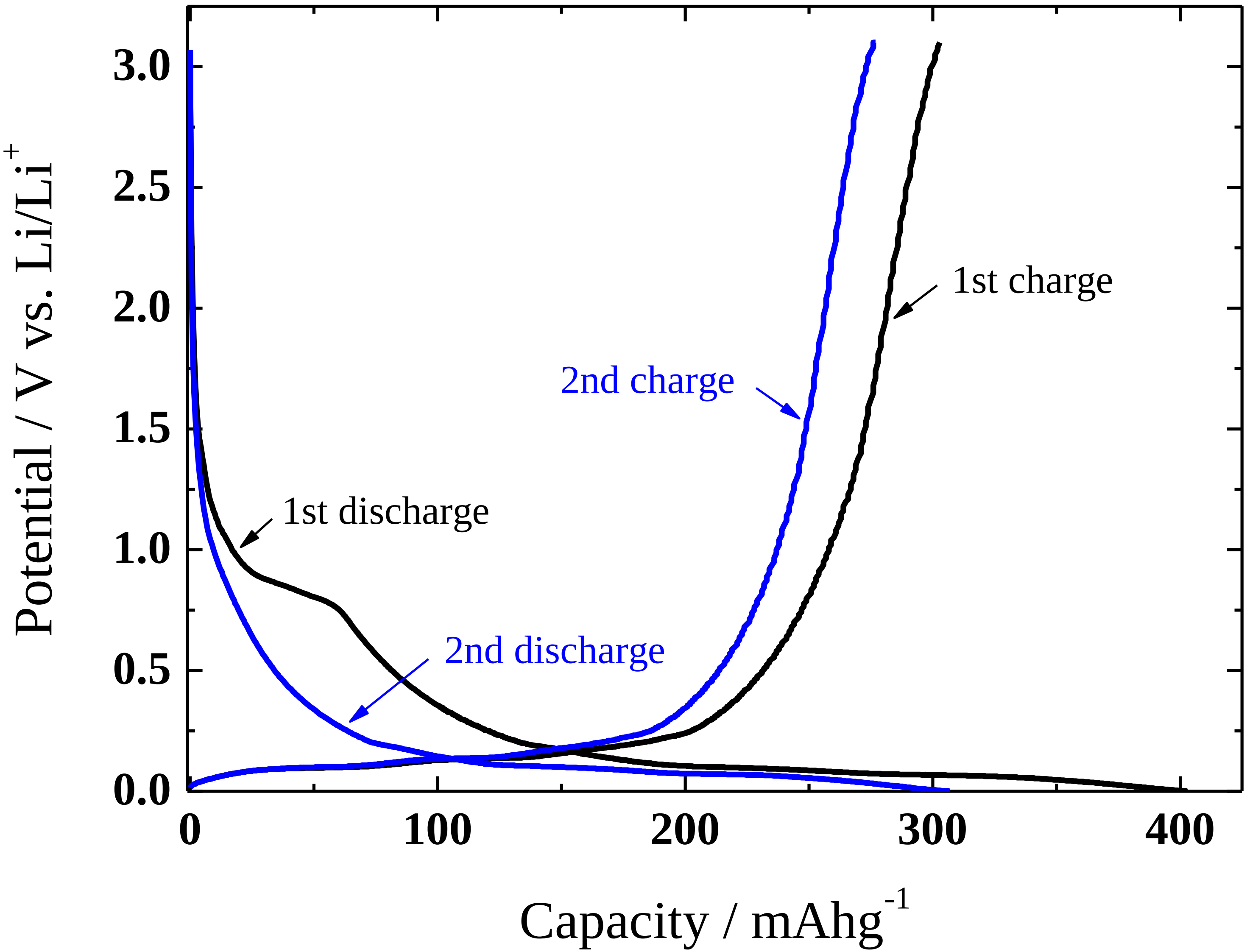
Intercalation of group 1 and 2 metals into B/C/N materials

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Ion diameter	180 pm†	232 pm†	304 pm†	172 pm†	228 pm†
BC_2N	1st stage*1,2 d_i = 370 pm	**1st stage*2 d_i = 430 pm**	1st stage*1,2 d_i = 542 pm	**2nd stage*4 d_i = 367 pm**	**2nd stage d_i = 430 pm**
BC_6N	1st stage*3 d_i = 365 pm	—	—	—	—
Graphite	1st stage d_i = 370 pm	**8th stage d_i = 450 pm**	1st stage d_i = 541 pm	**No intercalation**	**1st stage** d_i = 455 pm

Already used for the Li ion batteries

Under investigation for the Na ion batteries

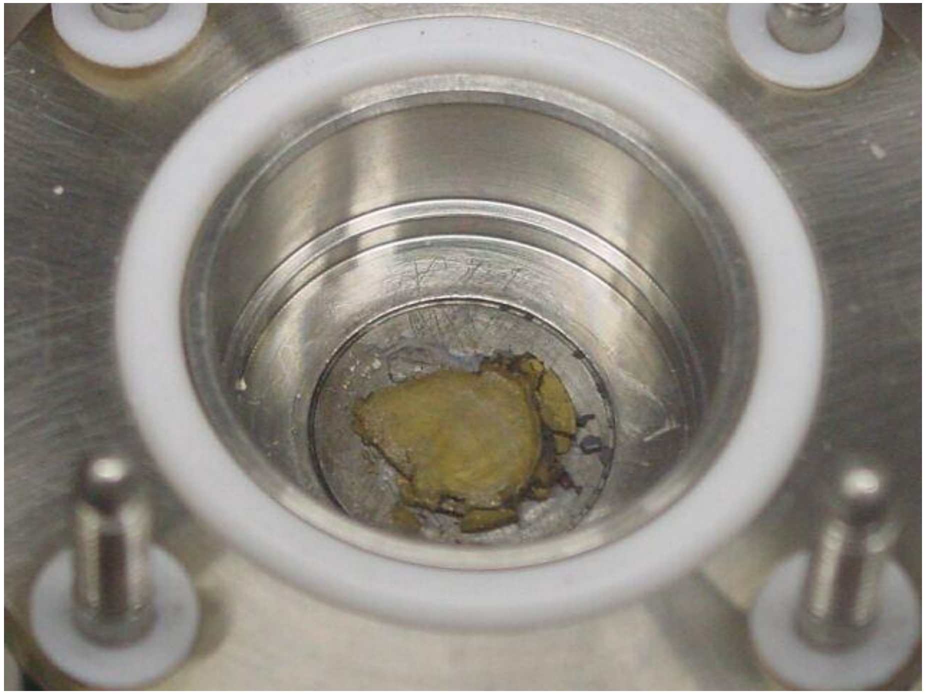
Hopefully Mg and Ca ion batteries in the future



Galvanostatic charge/discharge curves of the BC_6N prepared at 1470K in 1M-$LiPF_6$/EC+DEC. Current density: 100μA/cm^2.

Ref: M. Kawaguchi, Y. Imai and N. Kadowaki, *J. Phys. Chem. Solids* **67**(2006) 1084-1090.

1st stage Li-intercalated compound



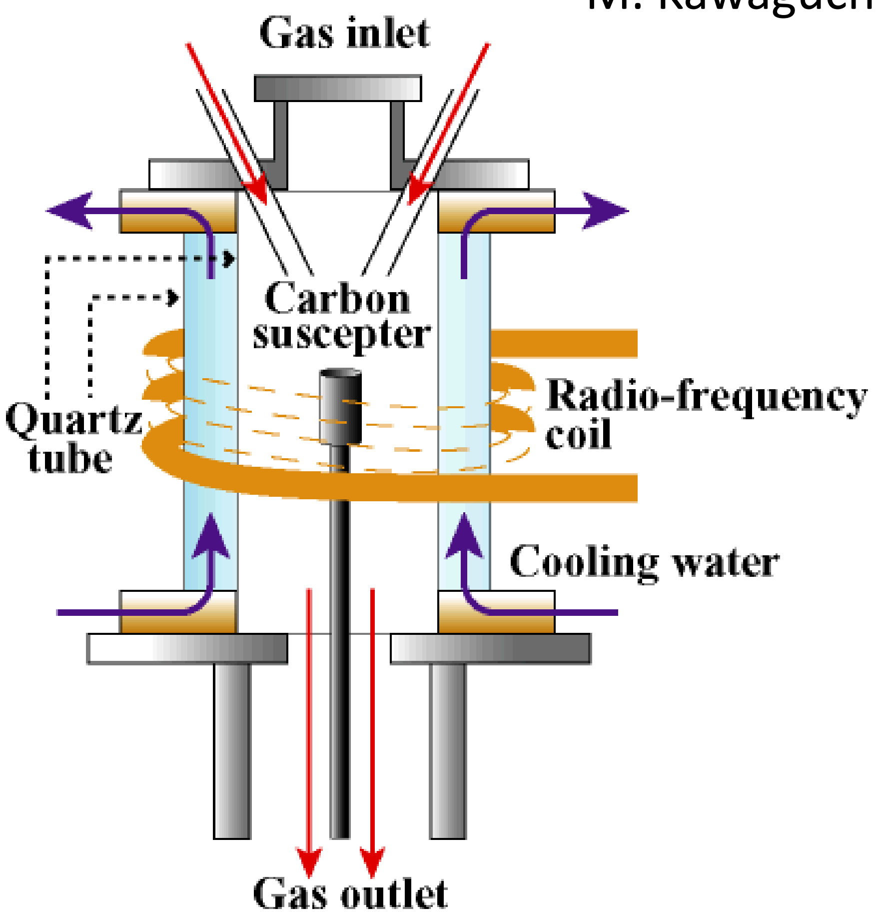
GIC: Li_xC_6

Li_xBC_6N

Preparation of BC_2N by CVD method

$$CH_3CN + BCl_3 \rightarrow BC_2N + 3HCl$$

J. Kouvetakis *et al.*, *Synth. Met.* **34** (1989) 1-7.
M. Kawaguchi et al., *J. Electrochem. Soc.* **157** (2010) 13-17.



Preparation condition

- Gas flow rate
  - CH_3CN (Acetonitrile) 40 ml/min
  - BCl_3 (Boron trichloride) 40 ml/min
- Reaction time
  - 120 min
- Temperature
  - 1470 K ~ 2070 K
- Pressure
  - 760 mmHg

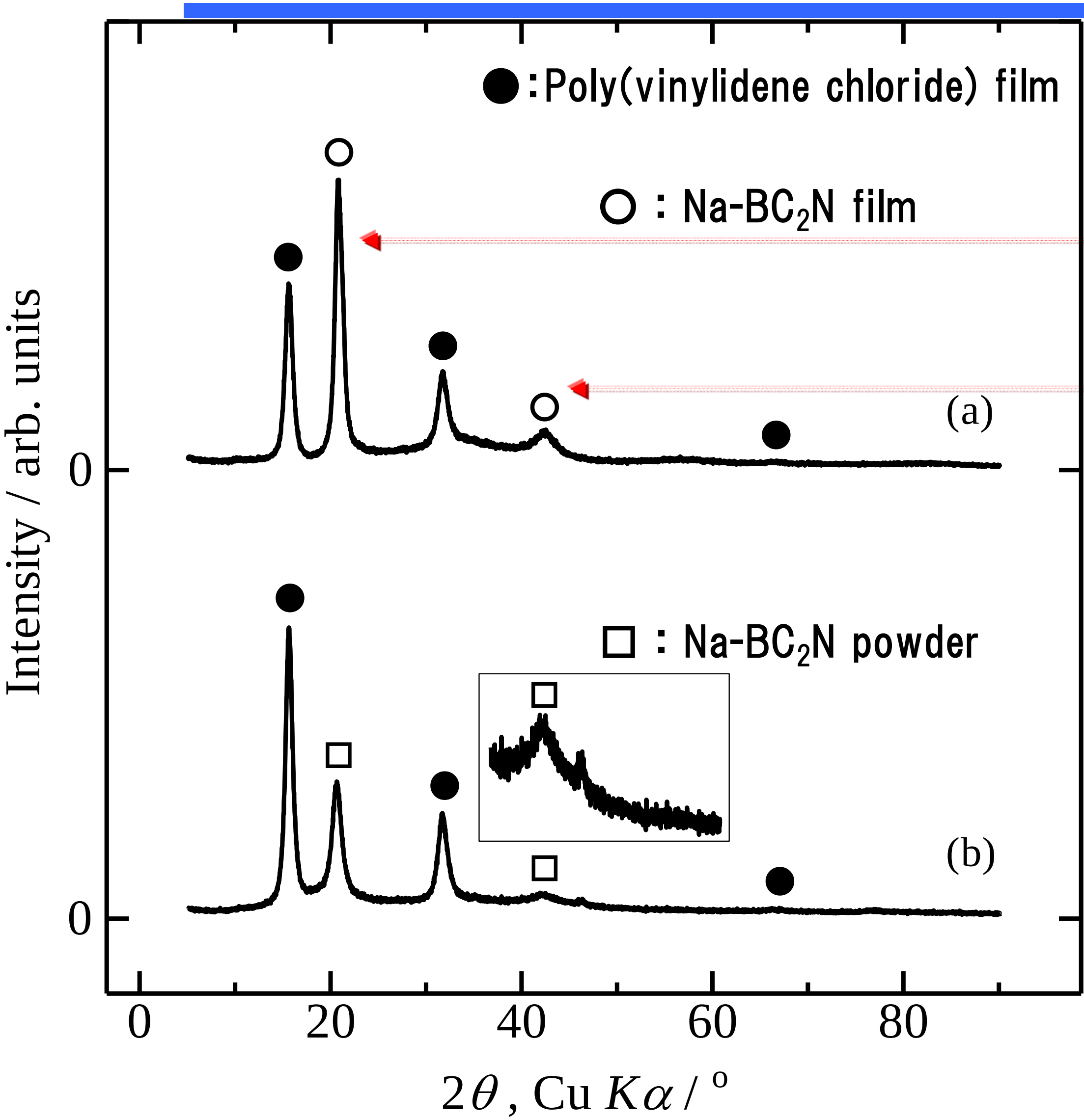
Intercalation of alkali metal into BC_2N

Two bulb method

Before the intercalation

After the intercalation
Ex: 620 K for Na intercalation

Na-BC_2N prepared by vapor phase reaction



d = 430 pm
(1st: 001)

d = 215 pm
(1st: 002)

Ref: M. Kawaguchi, et al., *J. Electrochem. Soc*, 157 (2010) P13-P17.

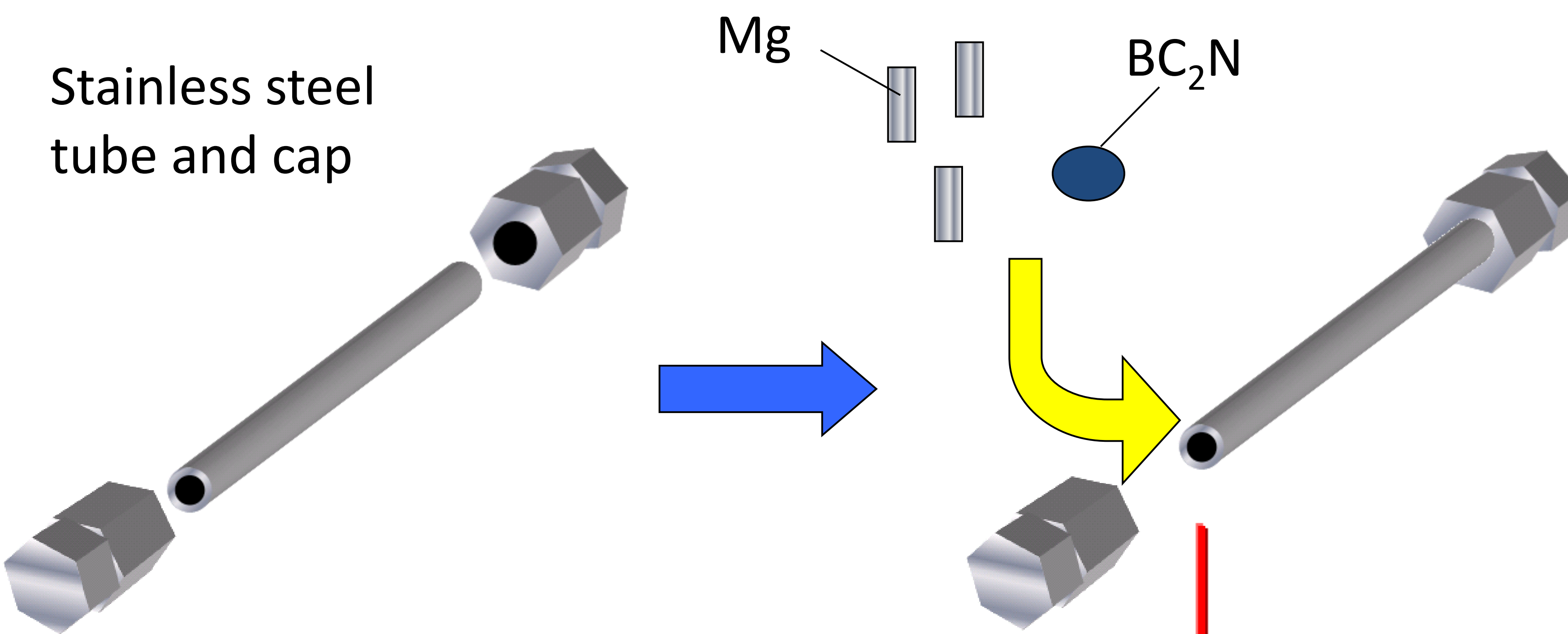
Na-GIC(8th stage)
Intercalated layer = 450 pm
Ref: R.C.Asher, J.Inorg.Nucl. Chem. 10 (1959) 238-249.

Interaction
Na-BC_2N > Na-GIC

X-ray diffraction pattern of Na-intercalated BC_2N (Reaction temp.: 620K. Host BC_2N was prepared at 2070K.

Intercalation of Mg into BC_2N

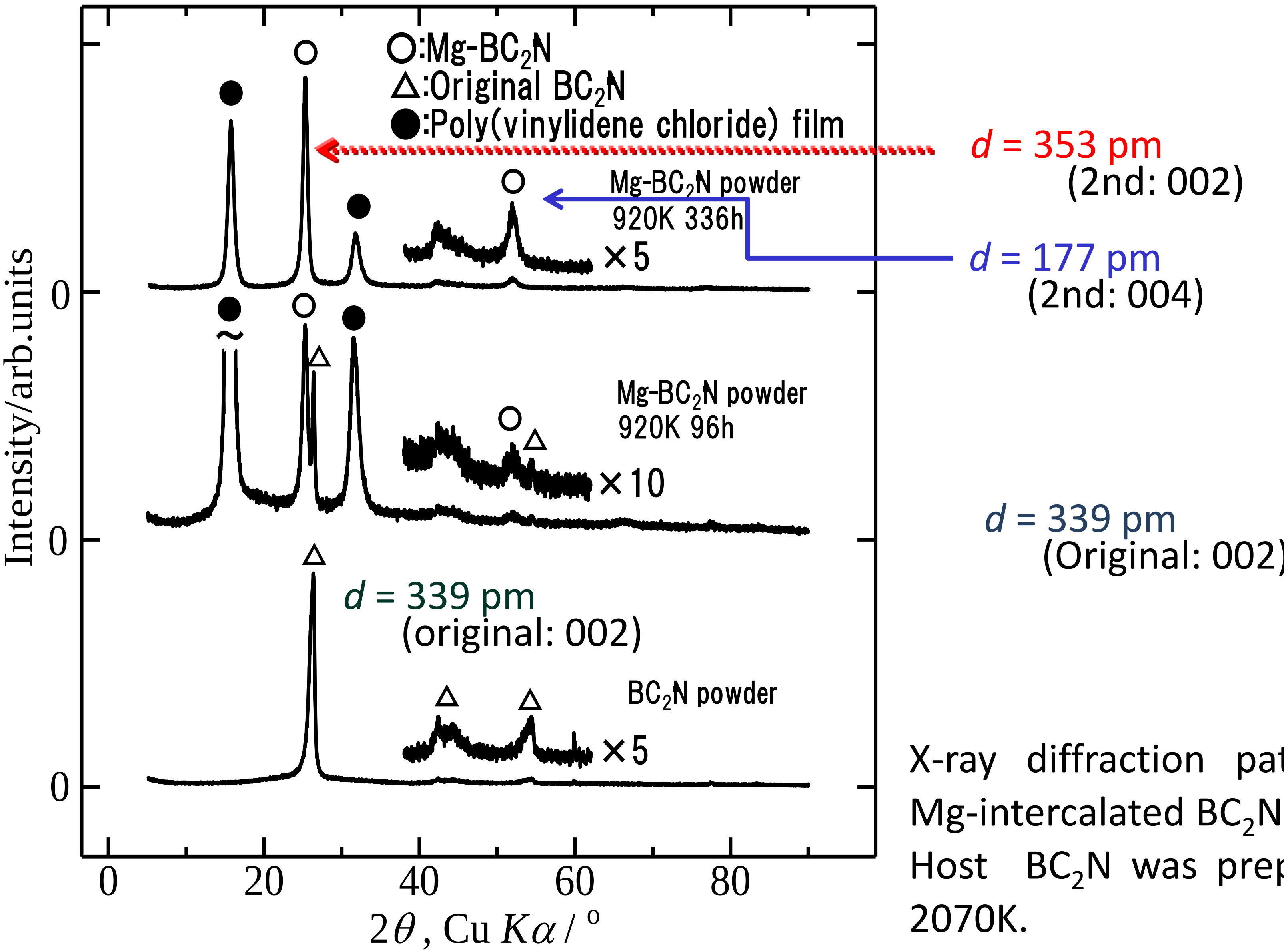
m.p. of Mg = 920K



Setting in a glove box
under Ar atmosphere

Heat-treatment in a furnace
at 920K

Mg-BC_2N prepared by vapor phase reaction

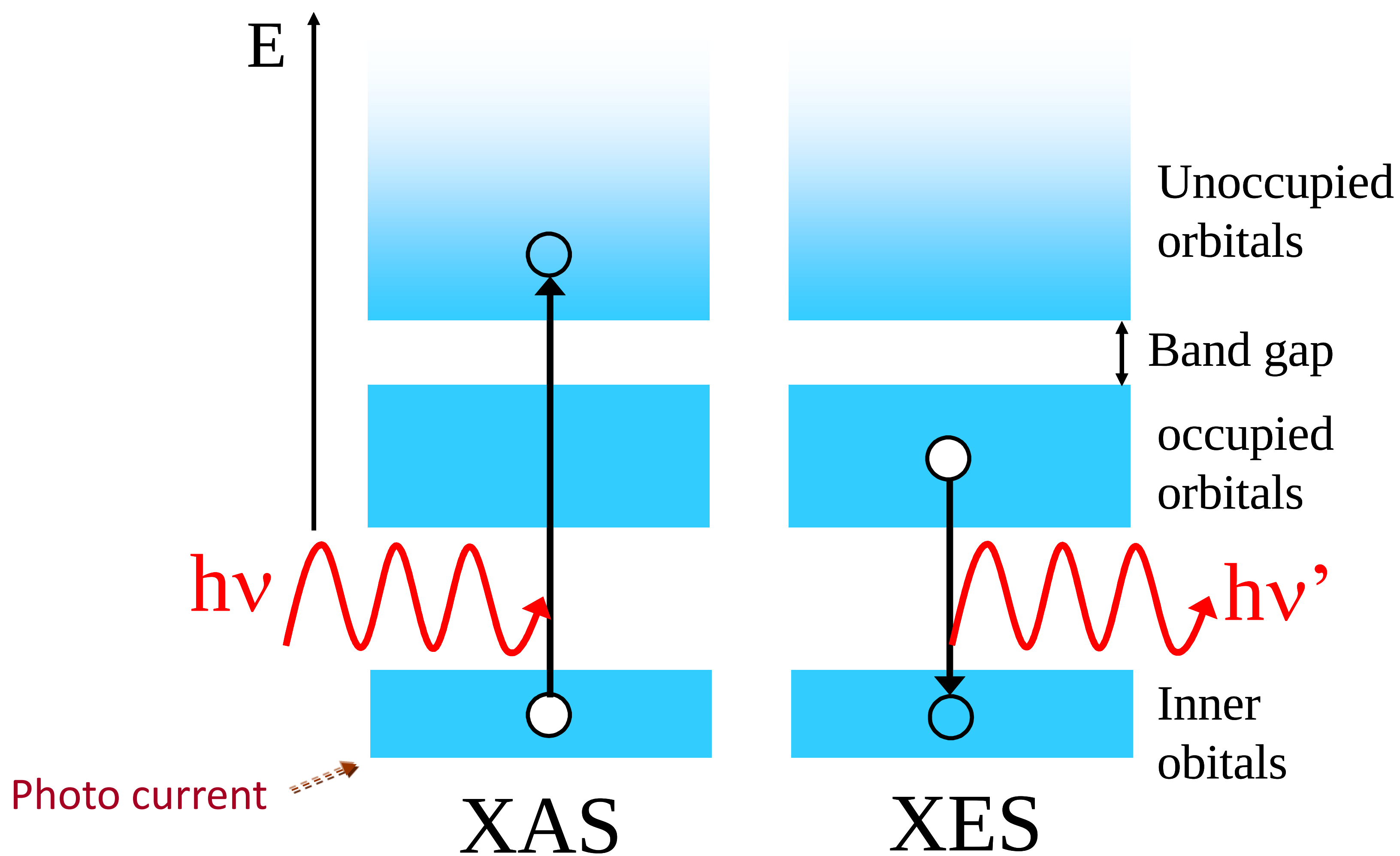


X-ray diffraction pattern of Mg-intercalated BC_2N.
Host BC_2N was prepared at 2070K.

Intercalation mechanism

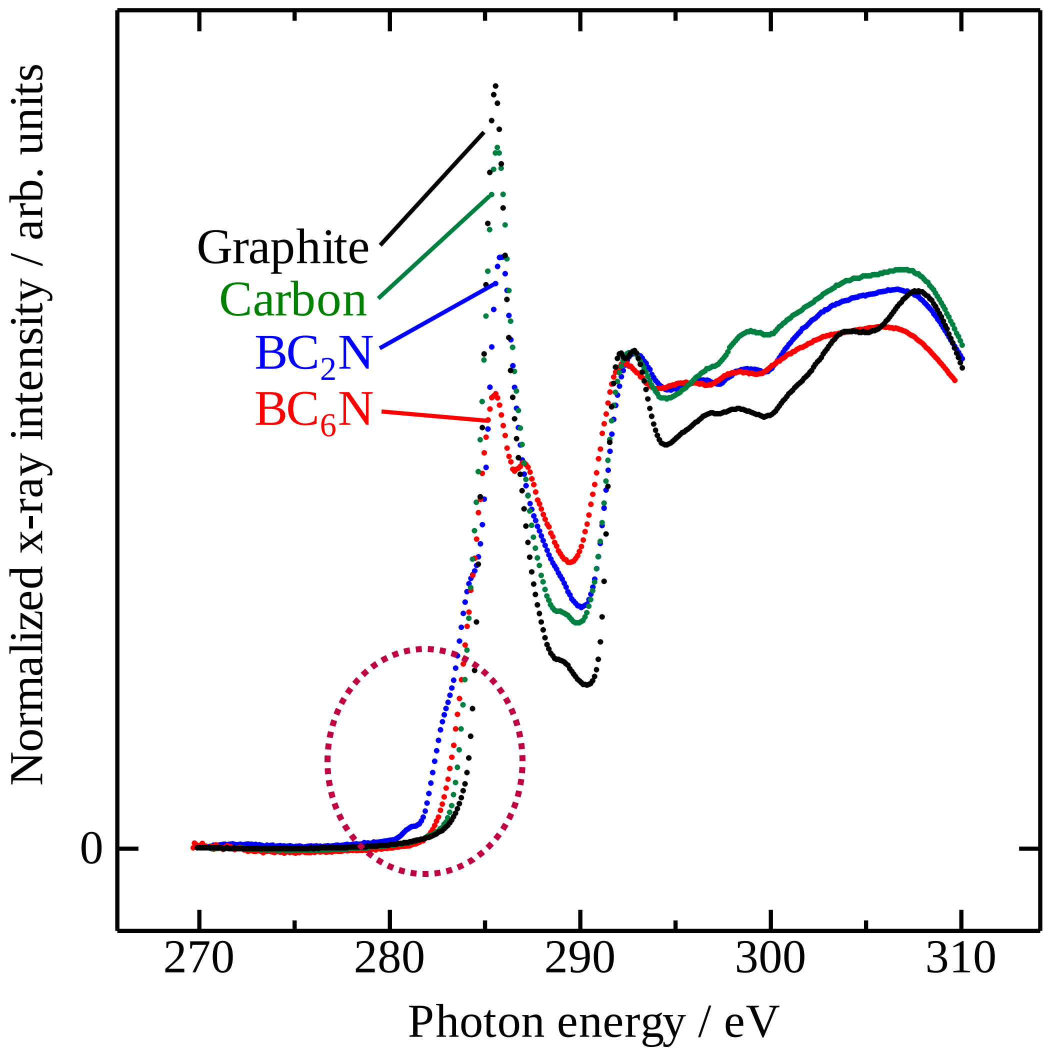
X-ray absorption (XAS) and emission spectroscopy (XES)

(Advanced Light Sources in LBL, California)



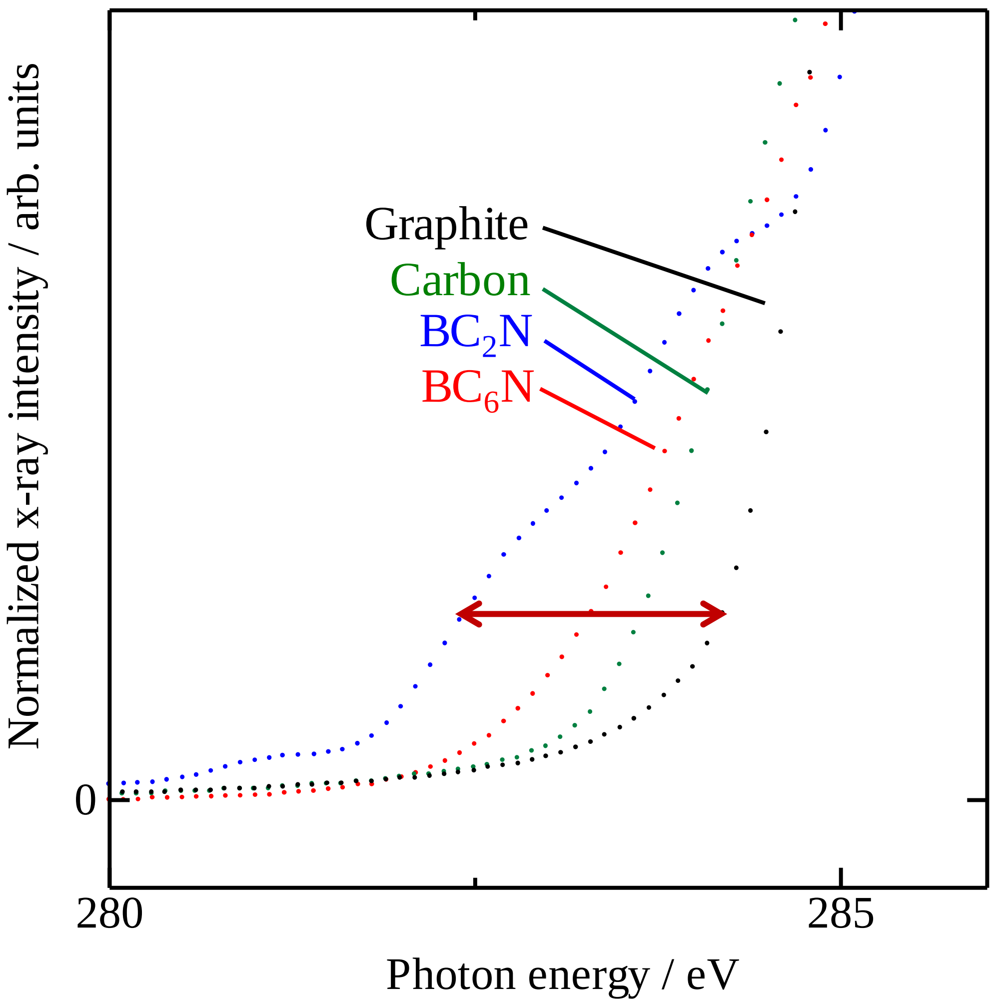
Total electron yield (TEY)

XAS spectra (C*K* region)



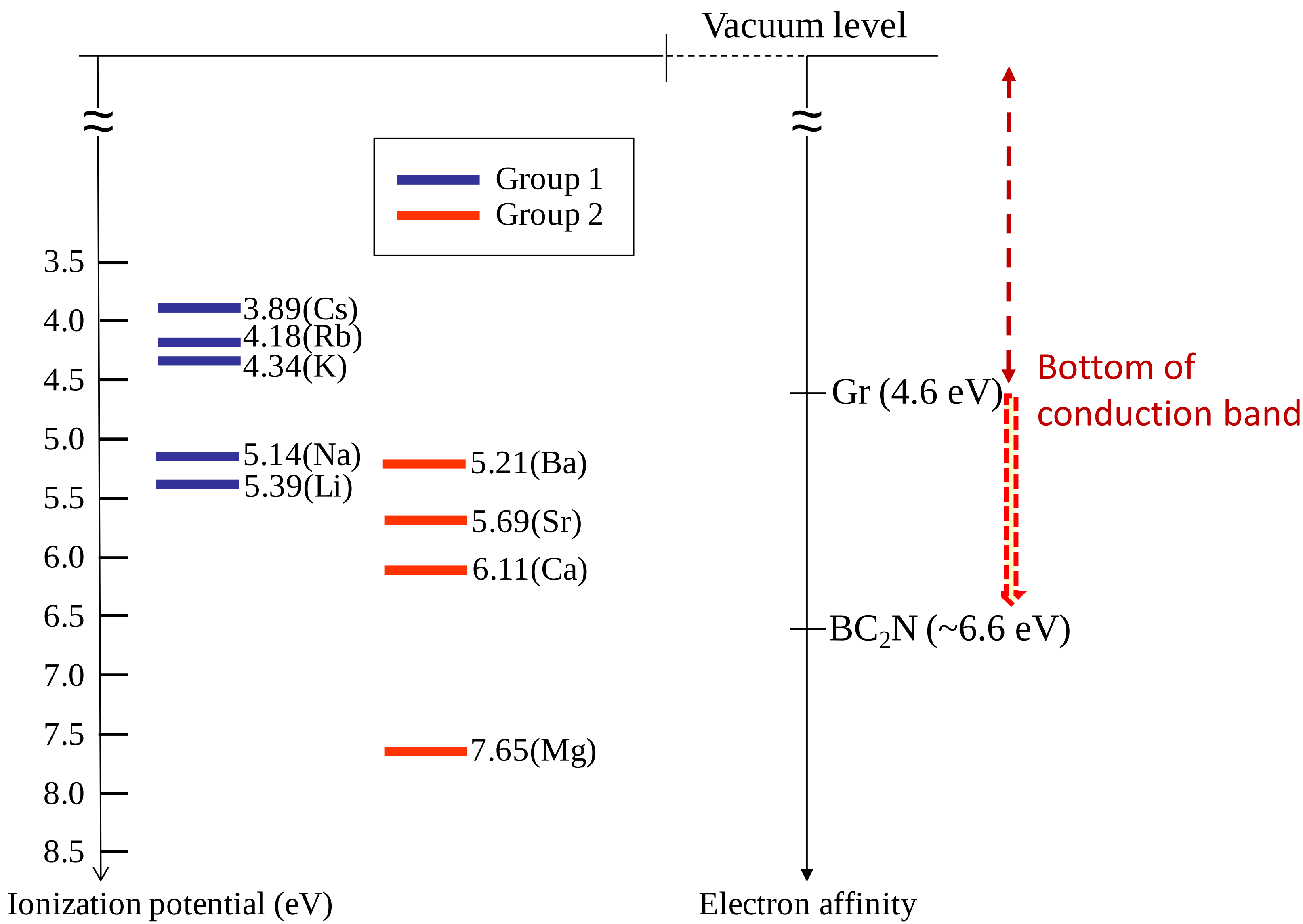
TEY X-ray absorption spectrum in the C*K* region of BC$_2$N film, compared with those of graphite, non-crystalline carbon and BC$_6$N. Incident angle:45°.

XAS spectra
(Low energy part in C*K* region)



TEY X-ray absorption spectrum in the C*K* region of BC_2N film, compared with those of graphite, non-crystalline carbon and BC_6N. Incident angle:45°.

Ionization potentials of metals and electron affinities of host materials



M. Kawaguchi, et al., Chem. Commun., DOI: 10.1039/C2CC31435E (2012).

Born-Haber Cycle

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

ΔH_f : Formation Enthalpy

S : Heats of Sublimation

D : Dissociation Energy

IE : Ionization Potential

EA : Electron Affinity

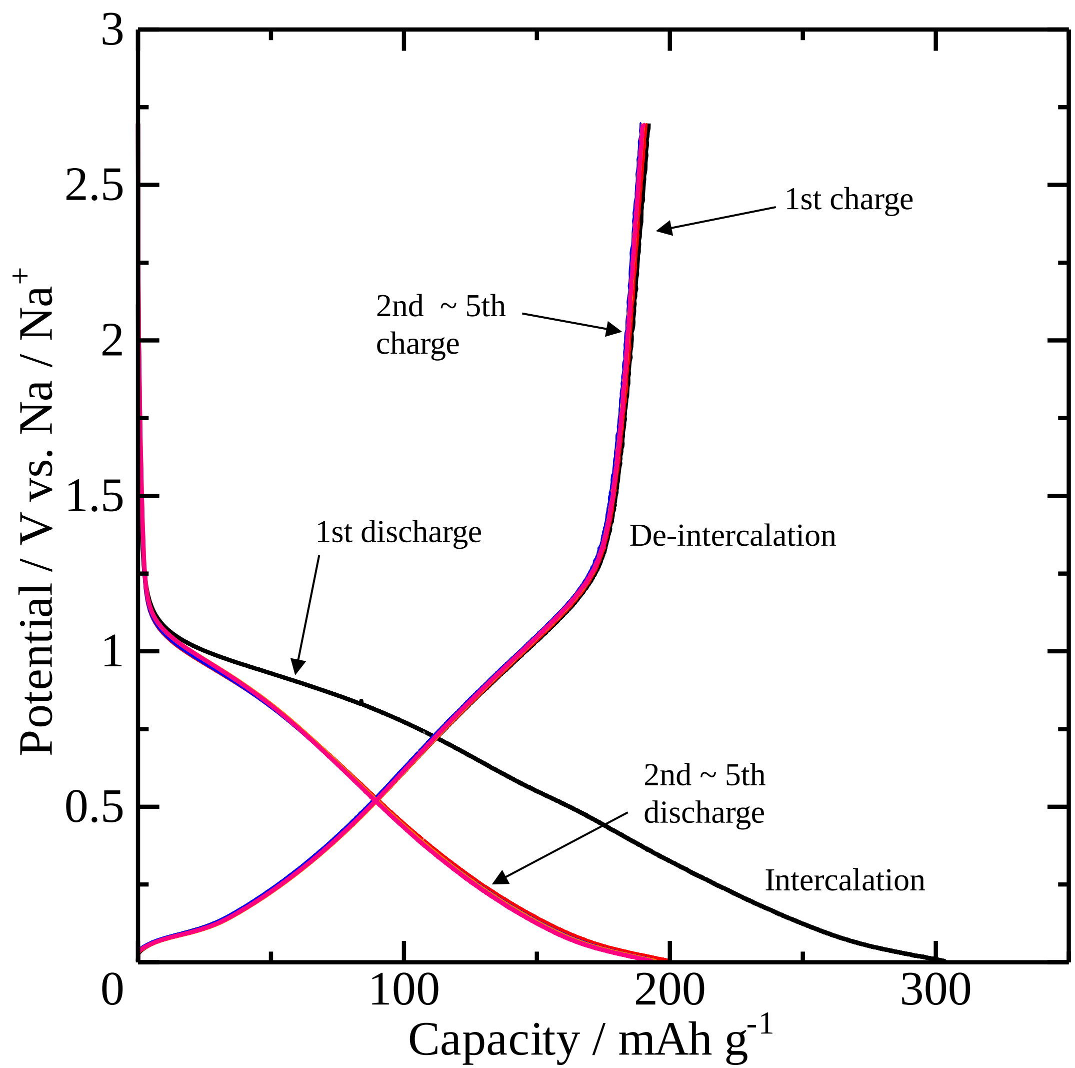
U : Lattice Energy

Mg^{2+}

$$U = -\frac{N_A M z_+ z_- e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

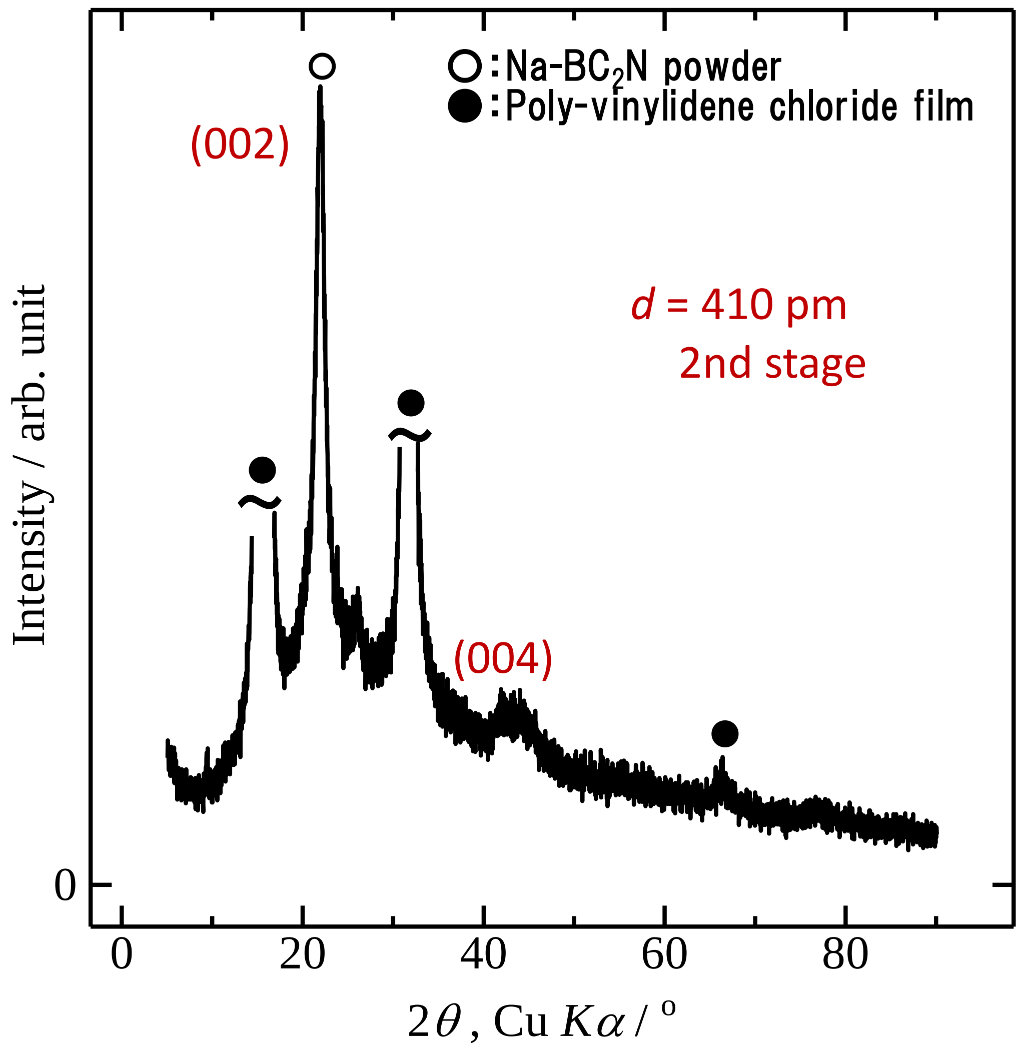
Application of intercalation to Na ion secondary batteries

Electrochemical intercalation of Na into BC_2N



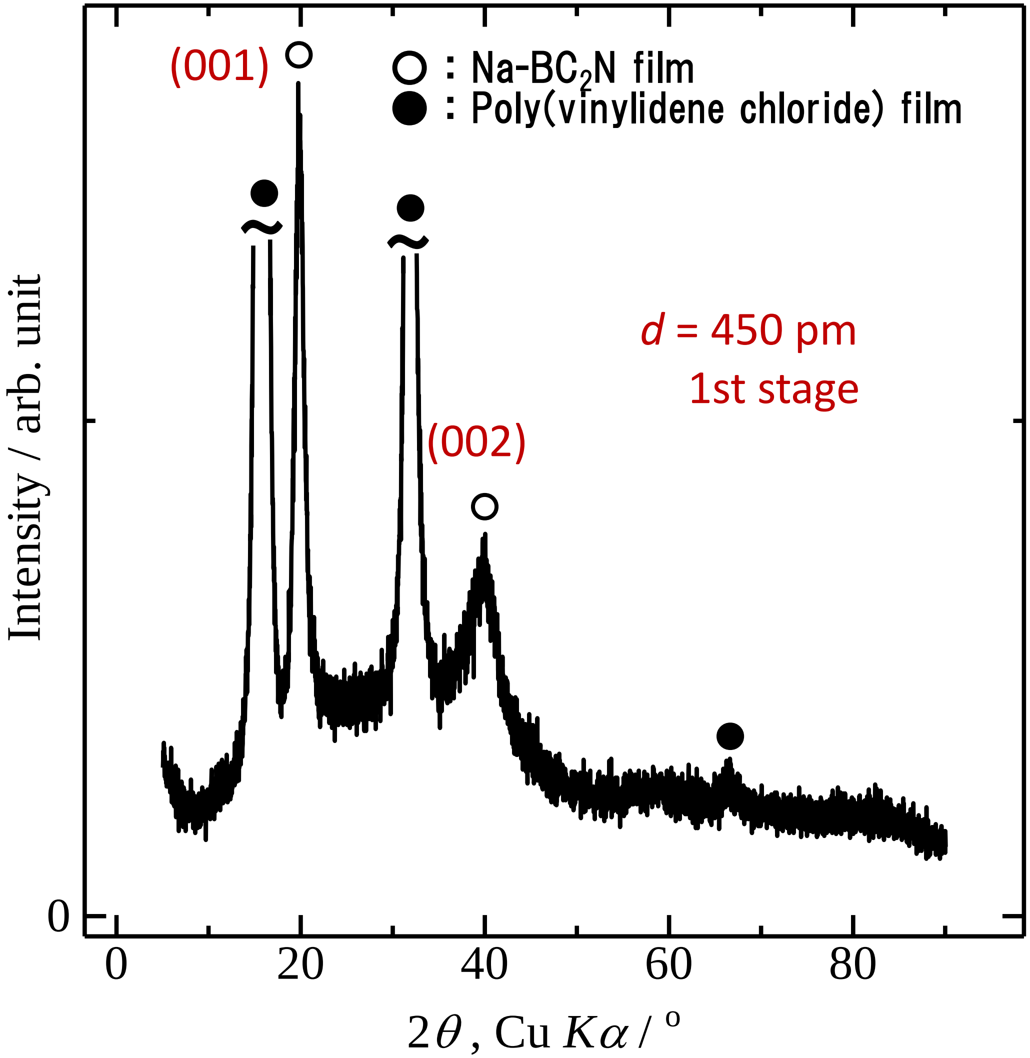
Discharge/charge curves of Na_xBC_2N by galvanostatic method in 1M-$NaPF_6$/ EC+DEC. Current density: 100 μA/cm^2. WE: BC_2N prepared at 1770K.

Na-BC_2N powder prepared by CCCV method



Na-BC_2N (0.7V vs. Na/Na^+) by CCCV method in $NaPF_6$/EC+DEC. WE: BC_2N prepared at 1770K.

Na-BC_2N film prepared by CCCV method



Low stage structure

Advantage ?

Graphite: Higher stage

Carbon: No stage structure

Na-BC_2N(full discharge: 0.003V vs. Na/Na^+

in $NaPF_6$/EC+DEC. WE: BC_2N prepared at 1770K.

Carbon Alloy（CA） ORR Catalysts (CAOC)

Discovered and named by the Gunma Univ. Carbon Laboratory

Introduction of

- Heteroatoms
- Structural defects
- Porosity
- ⋮

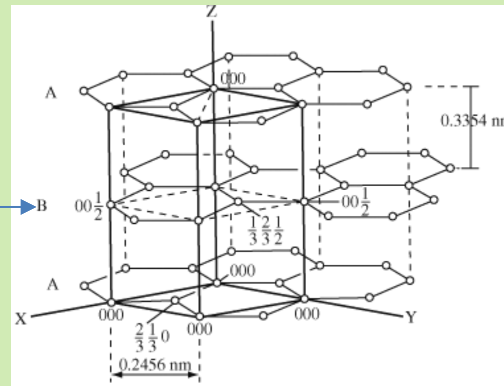
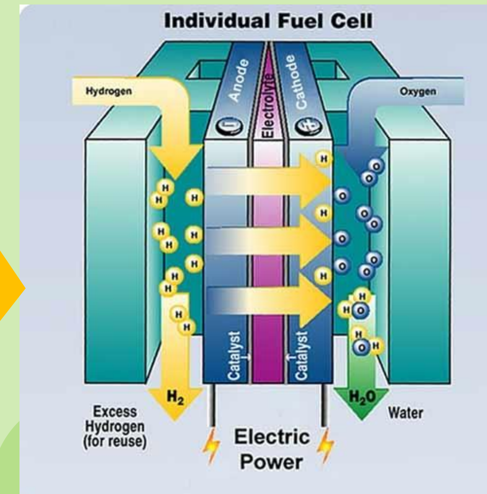


Figure 1. Representation of an ideal lattice of a graphite.

sp^2 dominant carbons



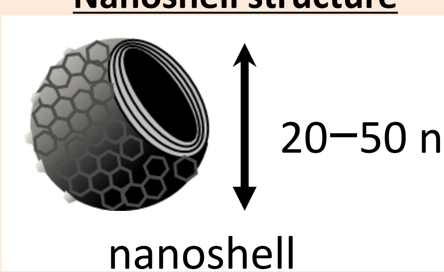
http://www.e2tac.org/e2tac/Research/EnergyStorage/FuelCells.aspx

Costdown

http://autoc-one.jp/motorshow/tokyo/2013/toyota/1553554/photo/0002.html

Two types of CAs by GUCL

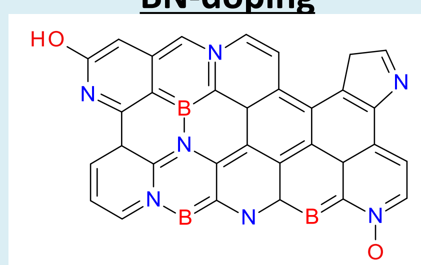
Nanoshell structure



Surface defects are important

N. Kannari et al. Carbon 50, 2941(2012)

BN-doping



B-N-C moiety is important

J. Ozaki et al. Carbon 45, 1847(2012)

Hetero-atom substitute carbon alloys: C/N materials

Preparation methods for C/N materials

CVD method → 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 → $(C_3N_3)_2(NH)_3$*, C_3N_4 type**

*M. Kawaguchi et al., *Chem. Mater.* **7** (1995) 257-264.

**M. Kawaguchi et al., *Chem. Lett.* (1997) 1003-1004.

Precursor pyrolysis method → C_xN*, C_3N, C_2N*****

*H. Konno et al., *Carbon* 35 (1997) 669.

**M. Kawaguchi et al., *J. Power Sources* 172 (2007) 481.

***M. Kawaguchi et al., *J. Electrochem. Soc.* 157 (2010) A35.

Template method → C_xN

G. Lota et al., Chem. Phys. Lett. 404 (2005) 53.

D. Hulicova, et al., *Chem. Mater.* 17 (2005) 1241.

C/N materials prepared by the present authors

Layered material **Yellow**

$2C_3N_3Cl_3 + 3NH_3 \rightarrow (C_3N_3)_2(NH)_3 + 6HCl$

Chem.Mater., 7, 257(1995). → Photoluminescence
Host material

C_3N_4 type: sp^3 hybridized

$C_3N_3Cl_3 + Li_3N \rightarrow C_3N_4 + 3LiCl$

Chem.Lett., 1003(1997).

White

CVD

$3CCl_4 + 16NH_3 \rightarrow C_3N_4 + 12NH_4Cl$

Carbon, 42, 345(2004).

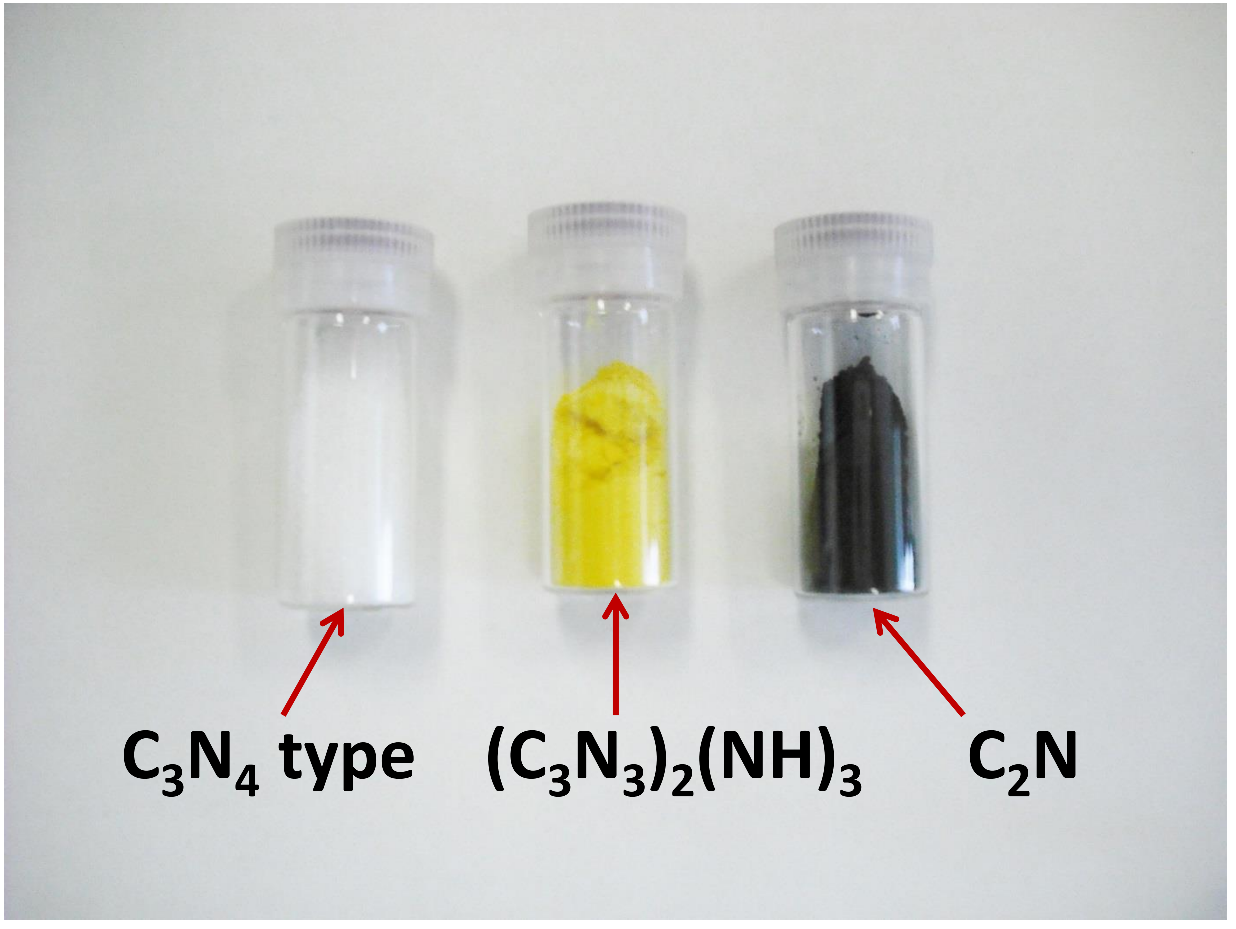
} Hardness
Photoluminescence

Layered material

$C_{10}N_8 \rightarrow C_6N_4\ (+\ 2C_2N_2) \rightarrow C_3N$ **Black**

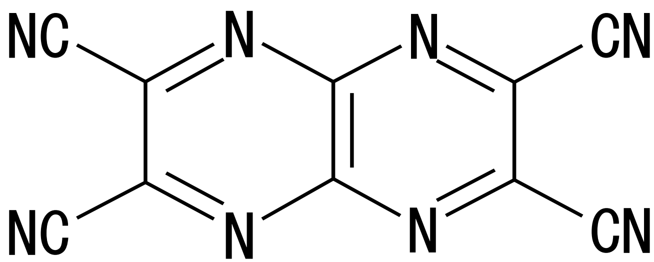
J. Power Sources, 172, 481(2007). → Electrochemical capacitor
Photo catalyst

Color of C/N materials



Application of C/N materials to capacitors

Preparation and application of C/N materials

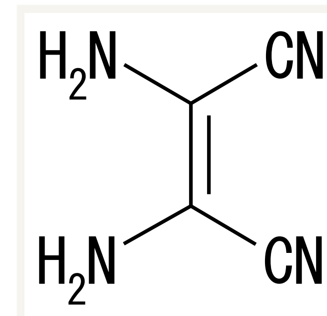


CAN： 2,3,6,7-tetracyano 1,4,5,8-tetraazanaphthalene

HT at 1070K

Composition：C_3N

Kawaguchi M, et al.,
J. Power Sources 2007; **172**:481-486.



AMN： diaminomaleonitrile

HT at 1020K

Composition：C_2N

Kawaguchi M, et al.,
J. Electrochem. Soc. 2010; **157**:A35-A40.

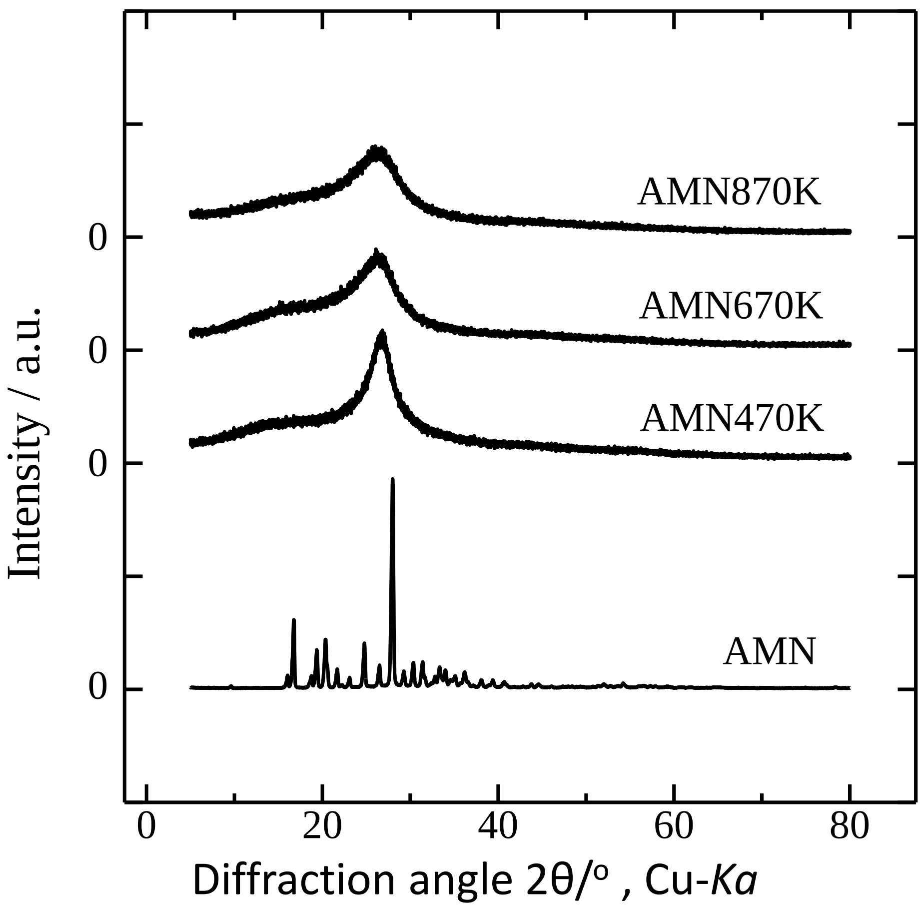
Application

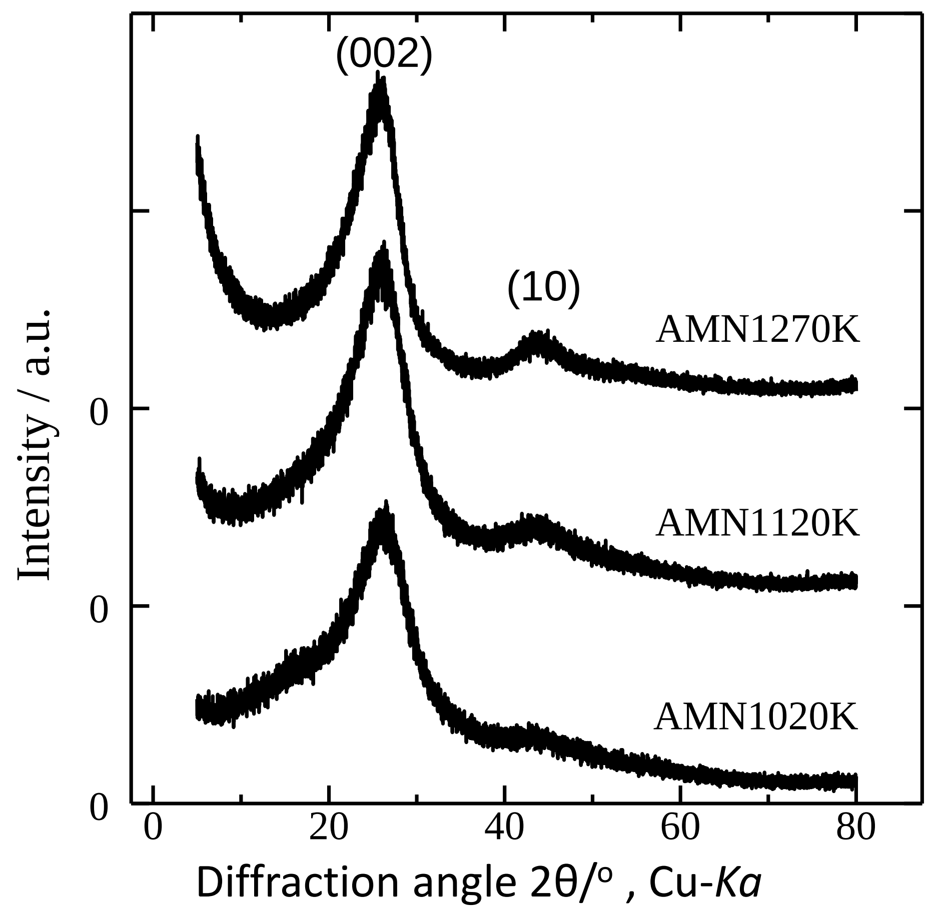
Capacitors

Adsorbents

Photo catalysts

Structure of C/N material





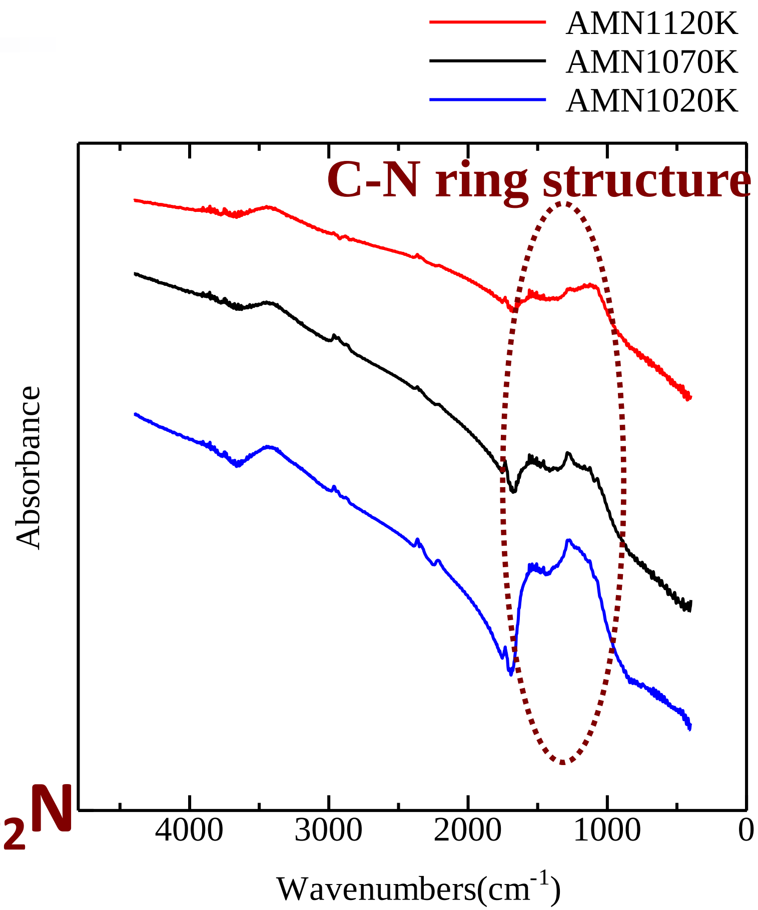
XRD patterns of C/N materials prepared by the pyrolysis of AMN at the temperature between 470K and 1270K.

Compositions of C/N material

Compositions of C/N materials prepared by the pyrolysis of AMN at various temperatures.

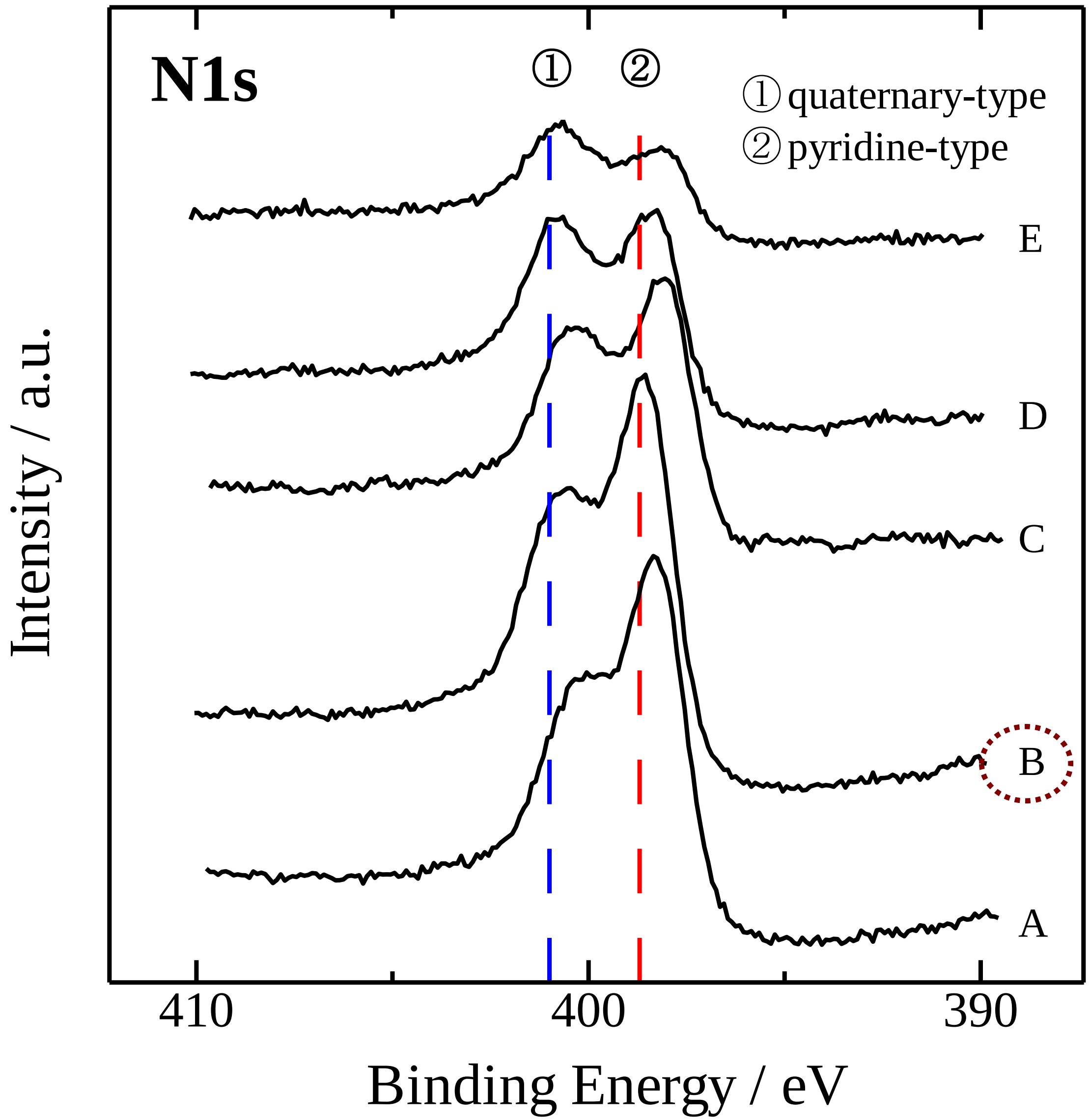
	C	N
AMN1120K	4.0	1.3
AMN1070K	4.0	1.7
AMN1020K	4.0	2.0
AMN	4.0	4.0

→ C_2N



FTIR spectra of C/N material

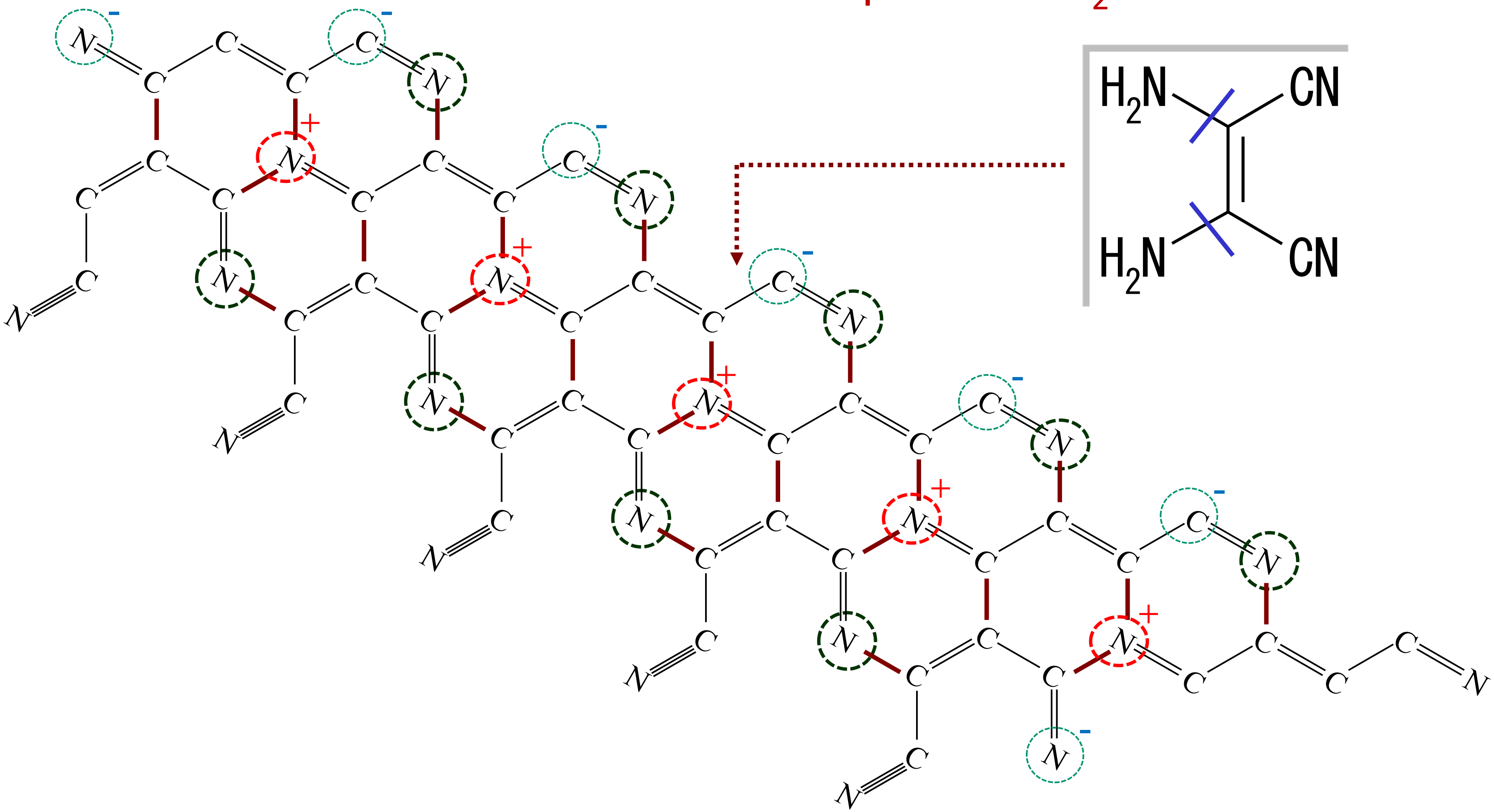
Chemical bonds in C/N material



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 → Composition: C_2N



Kawaguchi M, Yamanaka T, Hayashi Y, Oda H, J. Electrochem. Soc. 2010; **157**:A35-A40.

Comparison of CV curves

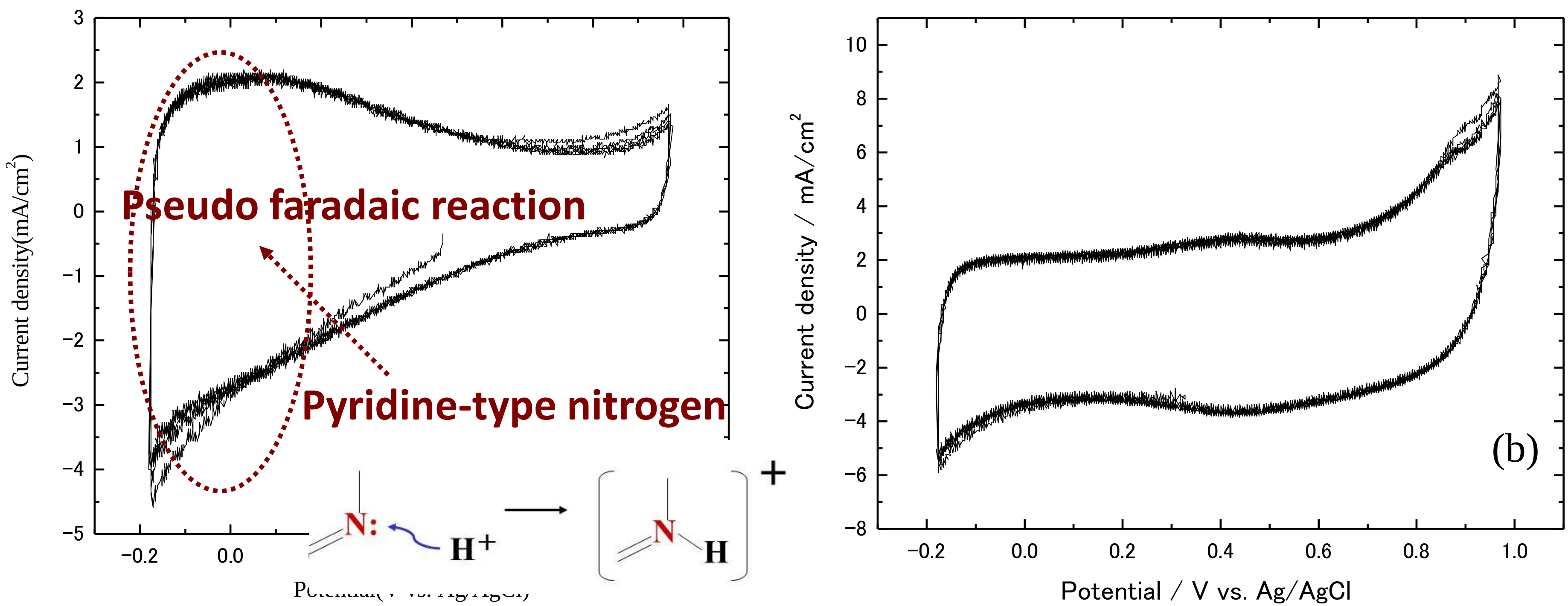


Figure Cyclic voltammograms for (a) C/N material prepared by the pyrolysis of AMN at 1020K (BET:230 m^2/g) and (b) activated carbon (BET:2300 m^2/g). 1M-H_2SO_4 aqueous solution. Scan speed:1mV/sec. Three electrode cell.

Kawaguchi M, et al.,
J. Electrochem. Soc. 2010; **157**:A35-A40.

Comparison of capacitive performances

	AC	C_3N	C_2N
Gravimetric capacity (F/g)	**180**	**160**	**200**
Specific surface area (m^2/g)	**2300**	**880**	**230**
Capacity per unit surface area (F/m^2)	**7.83×10^{-2}**	**18.2×10^{-2}**	**91.3×10^{-2}**
Apparent density (g/cm^3)	**0.34**	**0.68**	**0.65**
Volumetric capacity (F/cm^3)	**61**	**110**	**130**

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

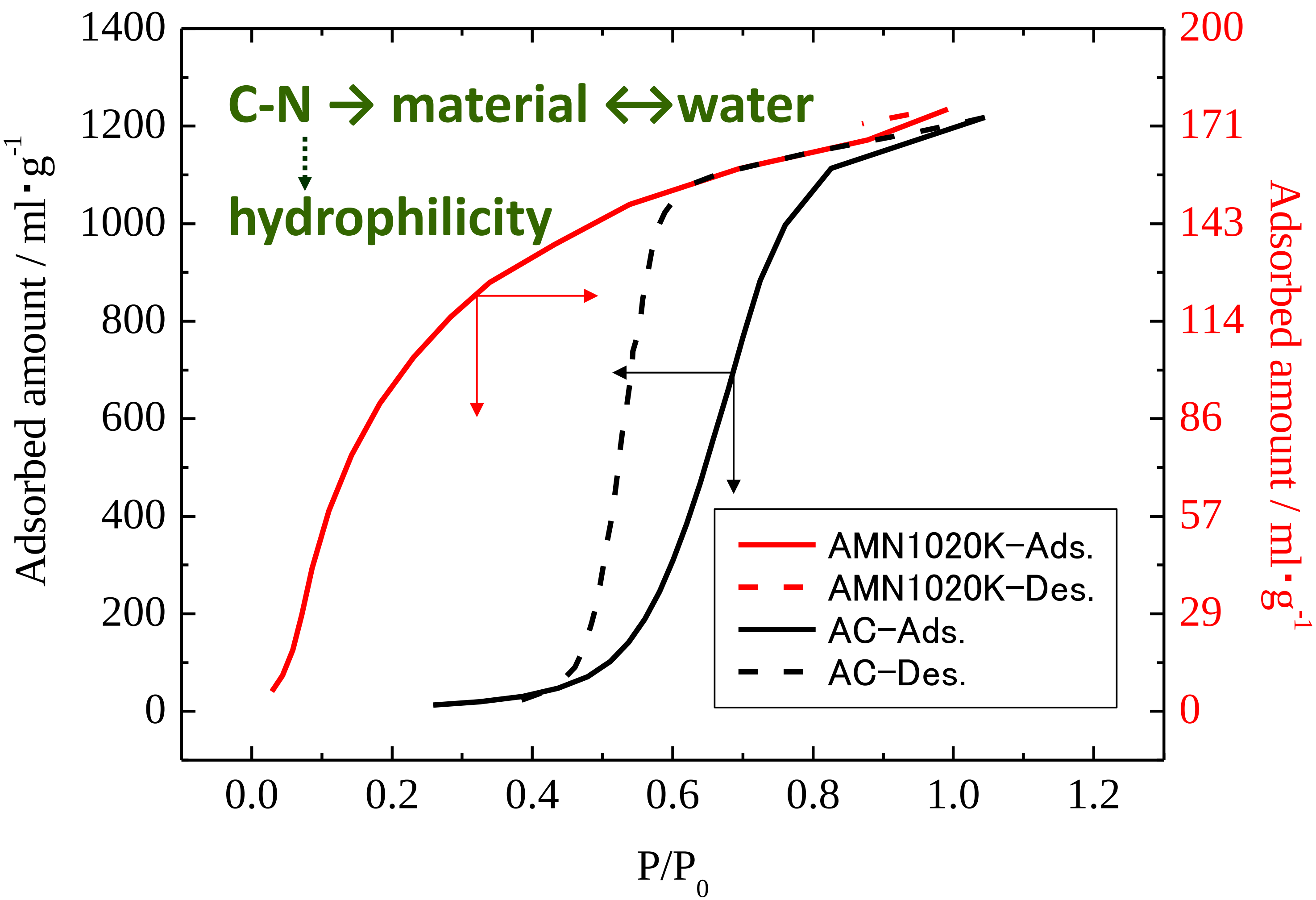


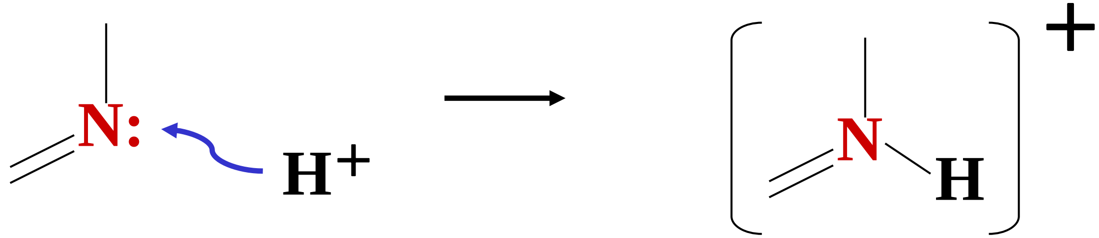
Figure Water adsorption isotherm (290K) of C/N material prepared by the pyrolysis of AMN at 1020K, compared with that of activated carbon.

Role of nitrogen in C/N material

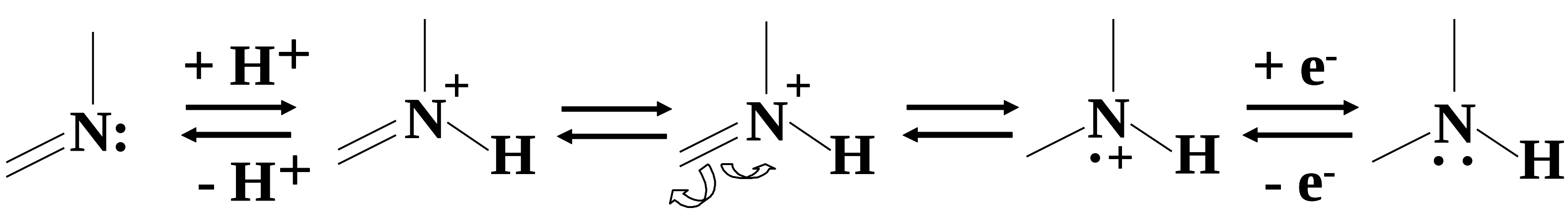
1) Increase in hydrophilicity by introduction of nitrogen → **Supply of ions into micro pores**

and

2) Interaction of pyridine-type nitrogen with protons



Addition of pseudo capacitance



Ref.: M. Kawaguchi, *et al.*, *J. Electrochem. Soc.*, 2010, 157, P13-P17.

Application of C/N materials to catalyst for electrolysis of water

Photo catalysts for H_2 production from water

- Metal oxides and nitrides: Maeda K., et al., J. Am. Chem. Soc., 2005; **127**,8286-8287.

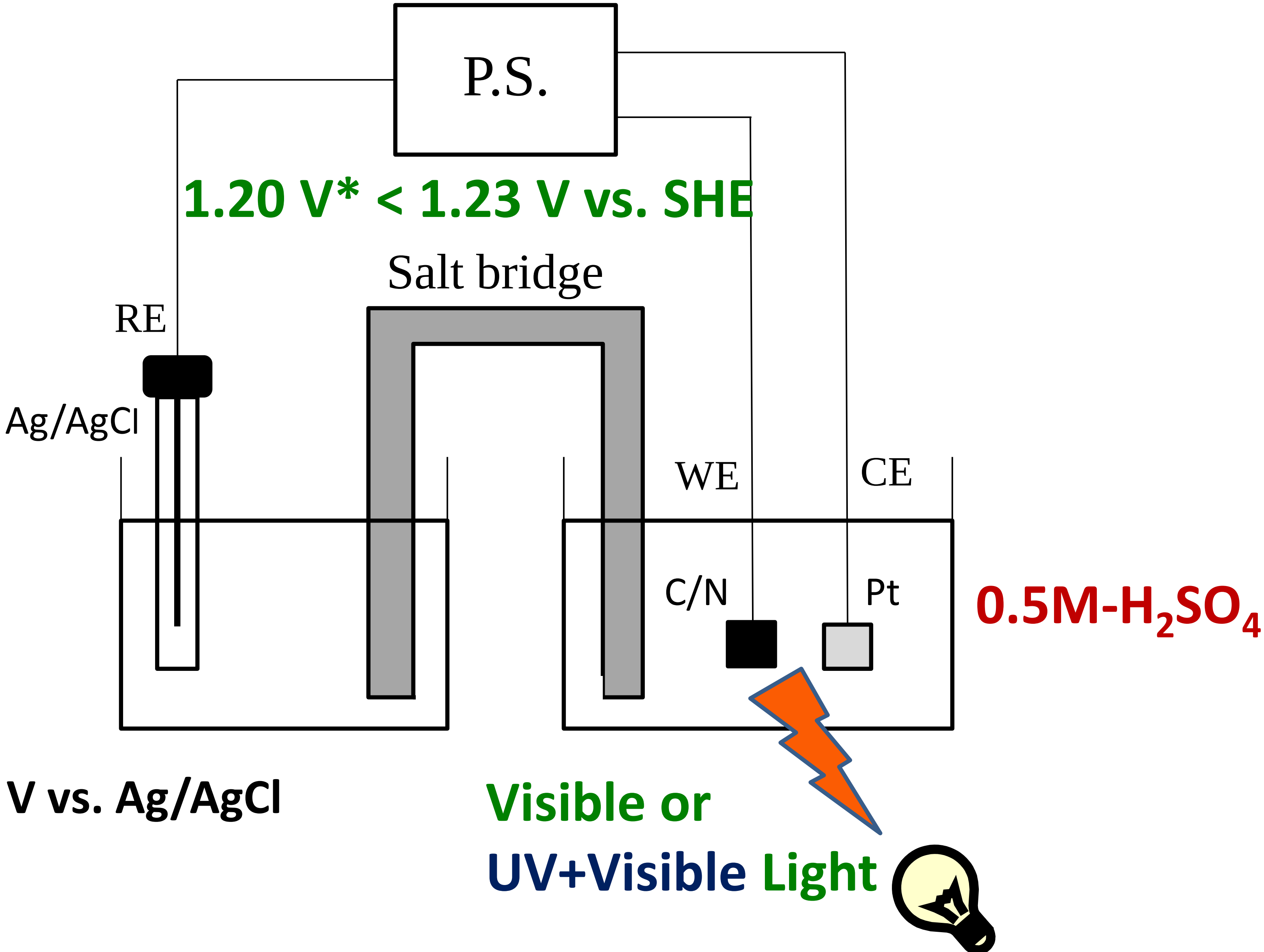
  A lot of researches

- C_3N_4 type: Wang X, et al., Nat. Mater., 2009; **8**:76-80.

  Not so many researches

3 wt % Pt was deposited on C_3N_4 for the supporting catalyst.

Apparatus for measurement of photo catalytic behavior



*1.00 V vs. Ag/AgCl

Photo Catalytic behavior of C_2N

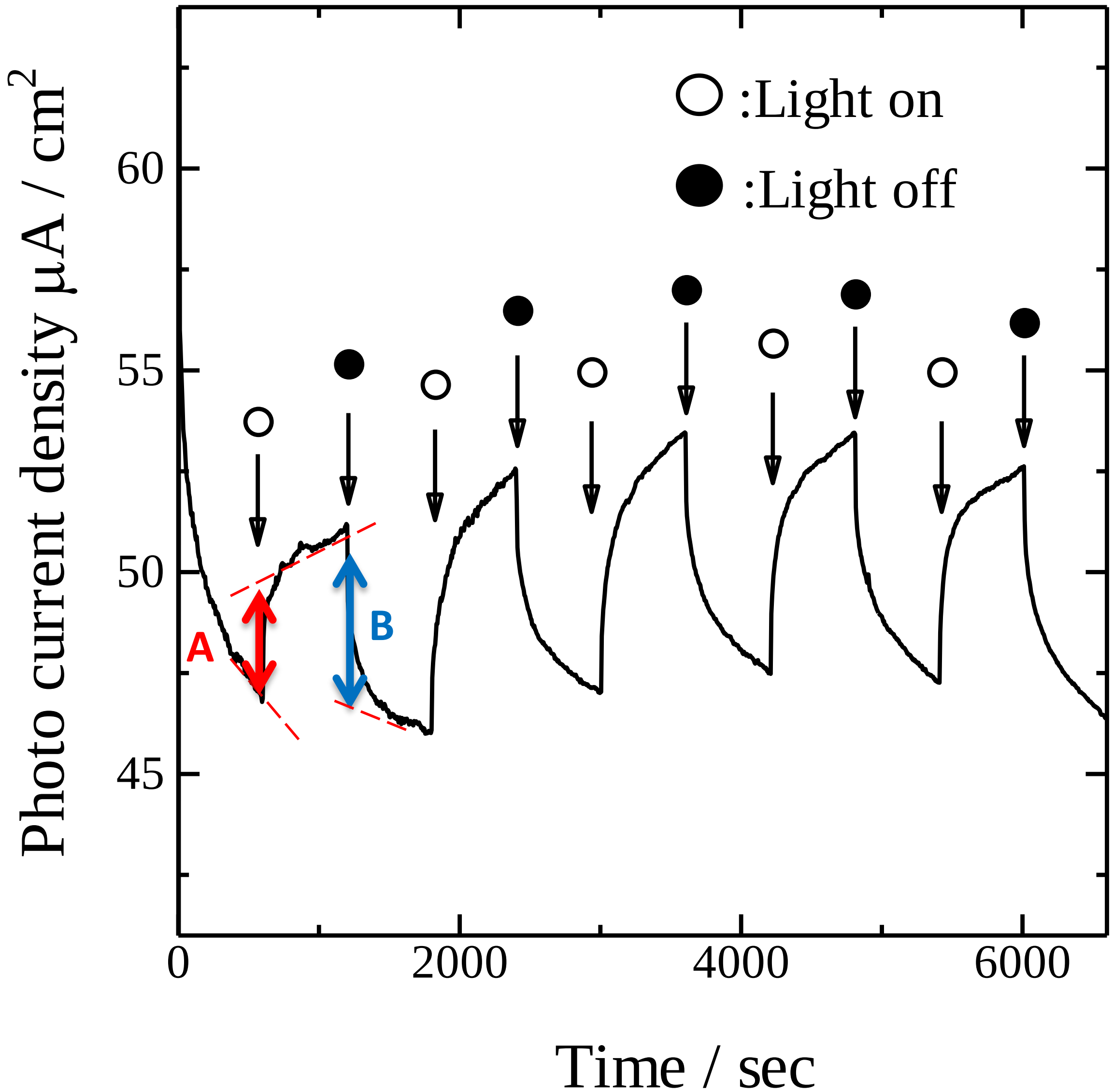
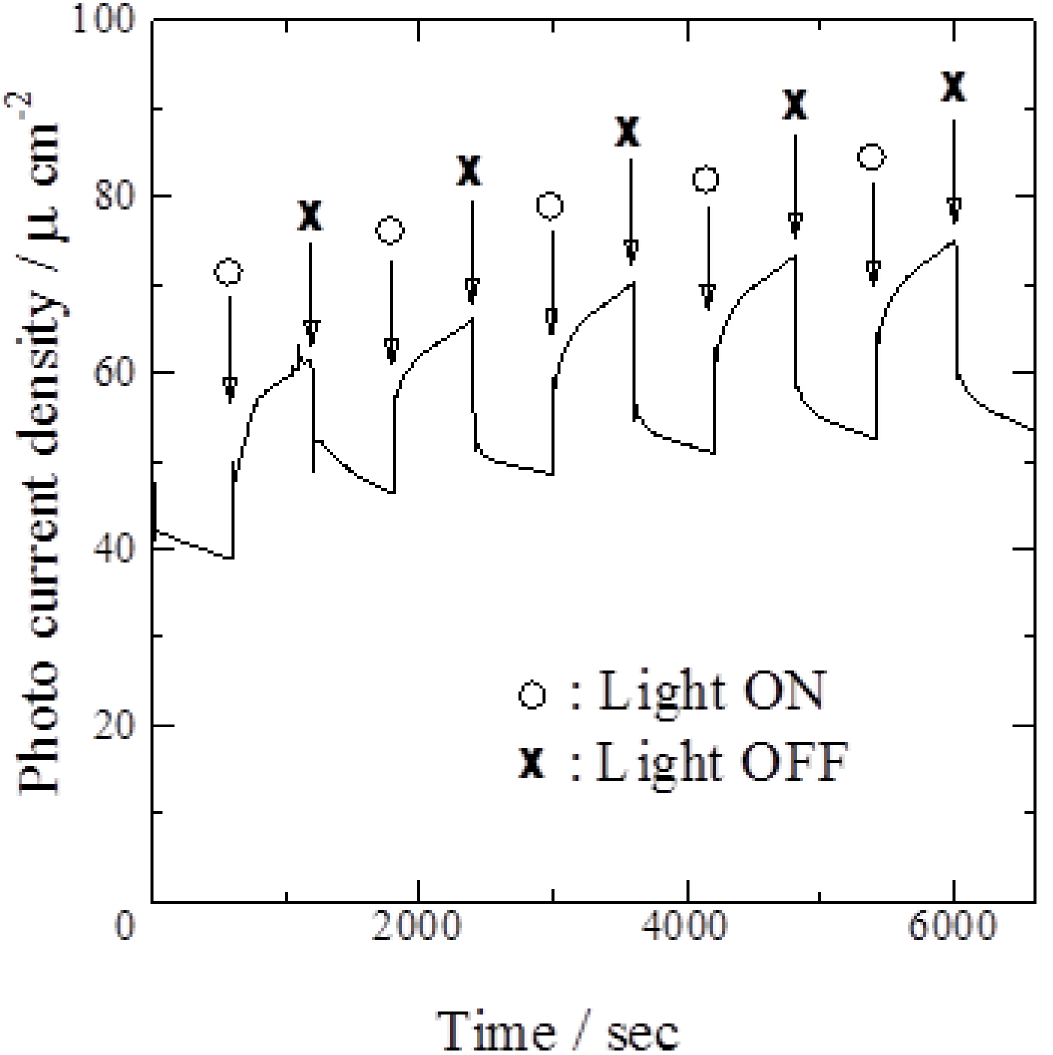


Photo current:

$$= \frac{A + B}{2}$$

Change in photocurrent for C_2N prepared from AMN in 1.0 M H_2SO_4.
The electrode was intermittently irradiated by visible light.

Photo Catalytic behavior of C_3N



Change in photocurrent for C_3N prepared from CAN in 1.0 M H_2SO_4.
The electrode was intermittently irradiated by visible light.

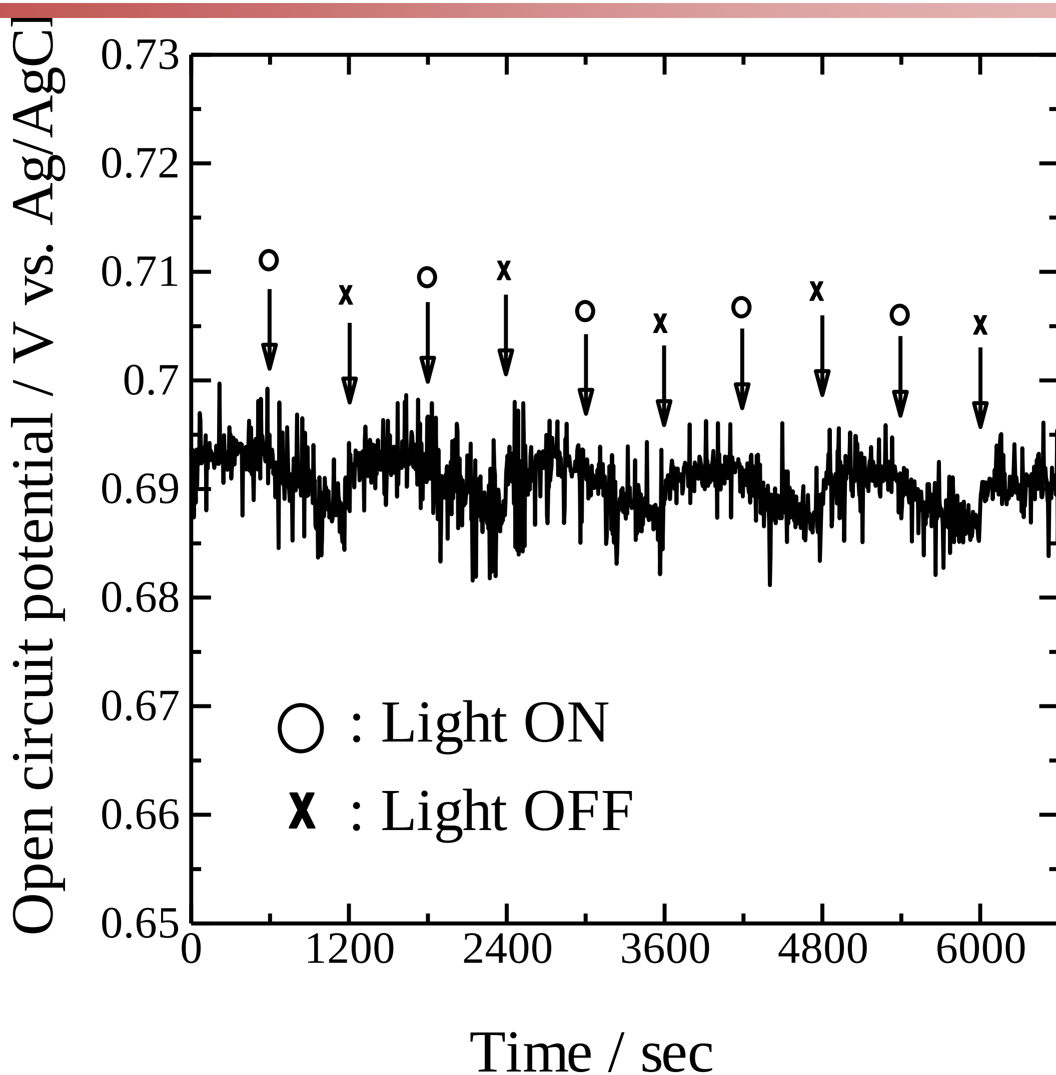
Comparison of photo catalytic current

Sample	Photo current density μA/cm^2	
	Visible light	UV-Visible light
TiO_2 (1200K)*	1.00	1.20
TiO_2 (870K)**	4.50×10^{-1}	2.73×10^{2}
TiO_2 (ST-01: powder)	1.35	2.78
C_2N (AMN1020K)	9.87	1.33×10
(AMN470K)	2.36	2.10
C_3N (CAN1070K)	1.28×10	1.55×10
(CAN670K)	1.47	5.26

*TiO_2 prepared on Ti plate at 1200 K

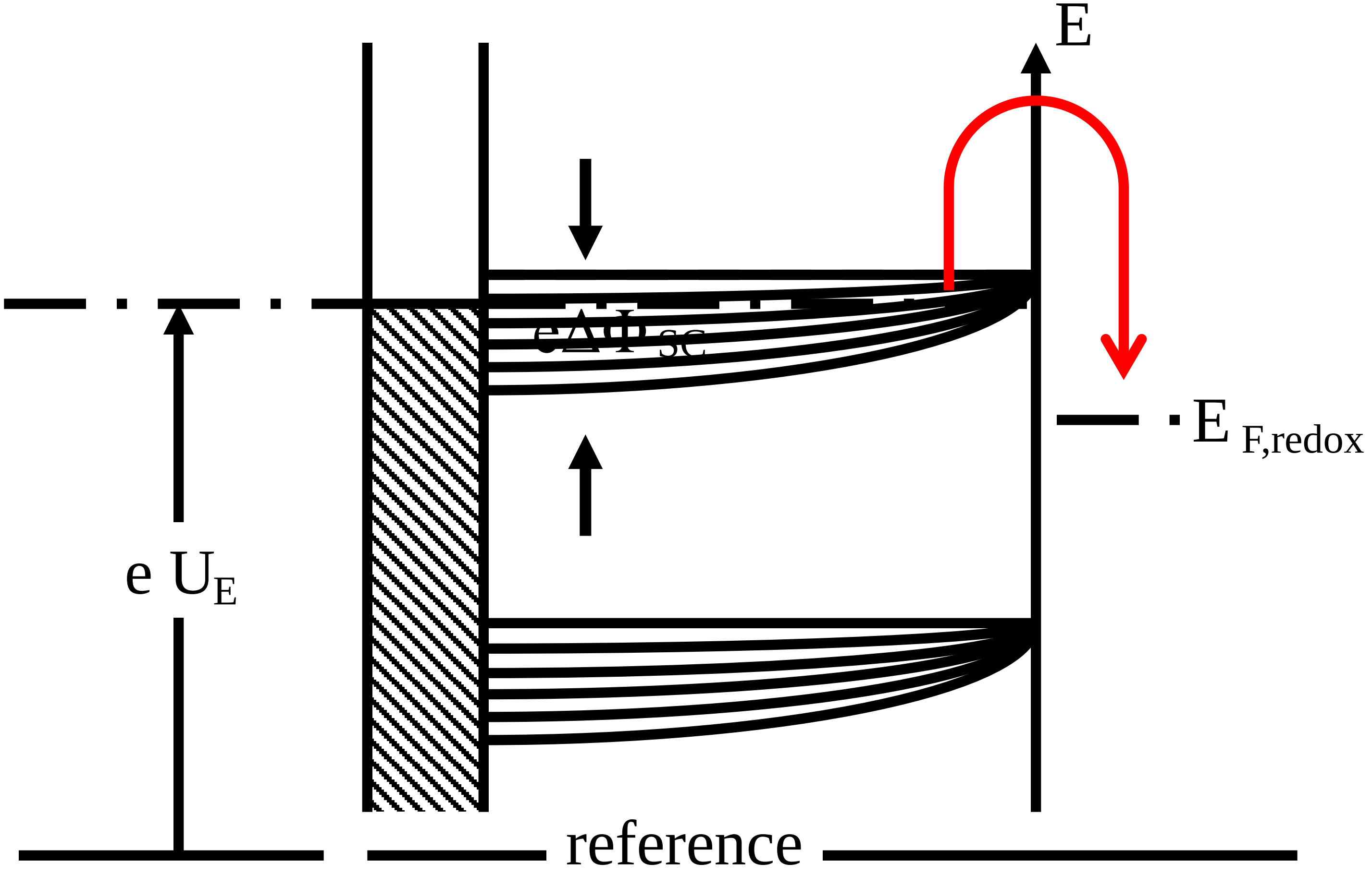
**TiO_2 prepared on Ti plate at 870 K

Photo catalytic behavior of C_3N

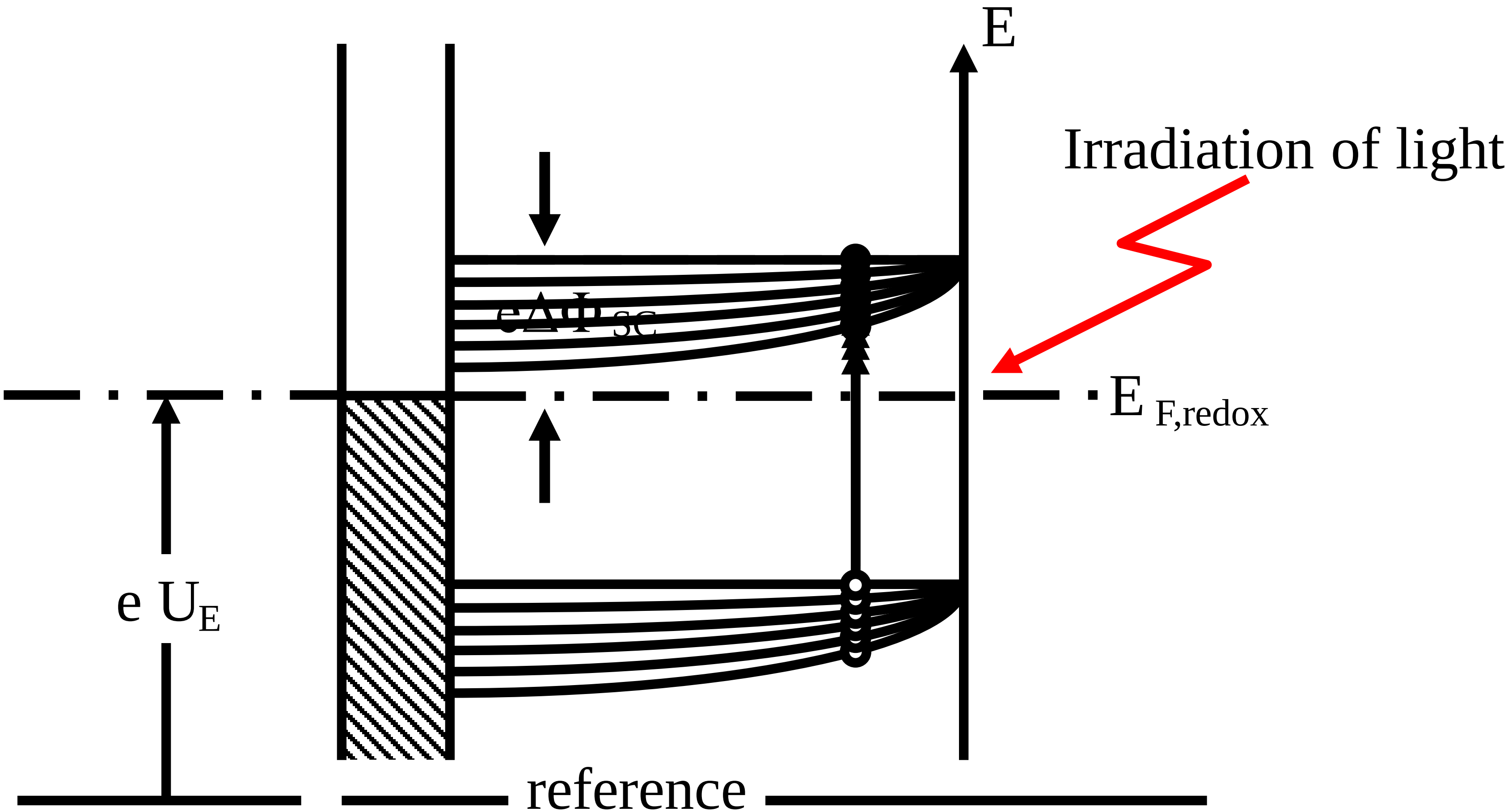


Change in open circuit potential for C_3N prepared from CAN in 1.0 M H_2SO_4.
The electrode was intermittently irradiated by UV with visible light.

Electronic structure of C_3N in H_2SO_4 aqueous solution



Electronic structure of C_3N in H_2SO_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.

Acknowledgements

Students (OECU):

Mr. Kaoru Yamada
Mr. Yuki Ishida
Mr. Hiromichi Ishikawa
Mr. Akihiro Kurasaki
Mr. Yushiki Hayashi
Mr. Takeshi Yamanaka
Mr. Yasuto Imai
Mr. Shinya Kuroda
Mr. Katsuya Onishi
Ms. Sayoko Yagi
Mr. Akinori Itoh

Helpful supports and advice:

Prof. Hirokazu Oda (Kansai U.)
Prof. Yasuji Muramatsu (U. Hyogo)
Prof. Noboru Akuzawa (Tokyo N.C.T.)
Dr. Masaya Kodama (AIST)
Prof. Hiroyuki Enomoto (OECU)
Mr. Hideaki Itoh (Nippon Soda Co.)
Prof. Claire Hérold (Nancy Univ.)
Prof. Sébastien Cahen (Nancy Univ.)

This work was partly supported by MEXT.KAKENHI (23350103, 19550197, and 11650865), Japan.

Thank you for your attention！

Danke schön!

ご清聴ありがとうございます！