Development of High Performance Carbon Anode Material

KURARAY CO., LTD.
Battery Materials Research Laboratory,
Kurashiki Research Center
Takafumi IZAWA
Outline

➢ Company Introduction

➢ Development of High Performance Hard Carbon
  1. Introduction
  2. R&D Road Map and request from market
  3. Enhancing capacity of HC by electrochemical method
  4. Enhancing capacity of HC by chemical reaction
  5. Summary
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Company Introduction ~Kuraray Co., Ltd~

- Established: June 24, 1926
- Capital: 89 billion yen
- Employees: 8,405 (consolidated, as of December 31, 2015)
- Net sales: 521.7 billion yen (consolidated, fiscal year ended December 2015)

Sales by Segment:

- PVA (film / resin)
- PVB (film / resin)
- EVOH (film / resin)
- Thermoplastic Elastomer
- Heat Resistant polyamide resin
- Liquid Rubber
- Acrylic thermoplastic elastomer

- Others: Liquid crystalline polymer film, Activated Carbon, membrane, waste water treatment
- Trading: Hook and loop fastener, Polyester, PVA fiber, high-strength polyarylate fiber
- Fibers and textiles: Artificial leather, Dental Materials, Methacrylic resin,
- Functional materials:
KURANODE™ is new type of hard carbon made from natural plant.

In addition to the superior characteristics of hard carbon, KURANODE has superior cost competitiveness and better handling property (lower moisture absorbency).
Company Introduction  ~Current Commercial Grades~

**Physical Properties**

<table>
<thead>
<tr>
<th></th>
<th>Type1</th>
<th>Type2</th>
<th>Type3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle size, $D_{v50}$</td>
<td>μm</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>m$^2$/g</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Interlayer spacing, $d_{002}$</td>
<td>nm</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>Crystallite size, $L_{c(002)}$</td>
<td>nm</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>True density*</td>
<td>g/cm$^3$</td>
<td>1.48</td>
<td>1.48</td>
</tr>
</tbody>
</table>

**Initial charge/discharge properties**

**SEM image**

- **Type1**
- **Type2**

**Charge capacity [Ah/kg]**
- **Type1**: 460
- **Type2**: 391
- **Type3**: 358

**Discharge capacity [Ah/kg]**
- **Type1**: 405
- **Type2**: 350
- **Type3**: 320

**Irreversible capacity [Ah/kg]**
- **Type1**: 55
- **Type2**: 41
- **Type3**: 37

**Efficiency [%]**
- **Type1**: 88
- **Type2**: 89
- **Type3**: 90

On the graph:
- **Potential (V vs Li/Li$^+$)**
- **Capacity (mAh/g)**

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Why Hard Carbon now?

- HC has great basic performances such as
  - Low temp. performance, Input / Output ability, Cycle ability etc.
  - Some of disadvantages of hard carbon such as moisture absorbency, cost etc. are improved by our development.
- Other anode materials (Graphite, Si etc.) also have some challenges.

Now HC is niche material but therefore there are still various undeveloped areas.

We may be able to have HC with
- Higher Volumetric Capacity
- Further High Power keeping existing superior basic performances.
R&D Road Map ~Applications and required performances~

**Customer demand**

- **LIC**
- **HEV**
- **PHEV**
- **EV or Consumer**

**Input-Output characteristic**

- **Type1**
- **Type2**
- **Type3**

**KURANODE™**

- **Gr + HC**
- **Graphite (Gr)**
- **Gr + Si**

**KURARAY**

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Developmental Products (Type A, B, C and Fully-Charged method)

Input-Output characteristic

- LIC
  - Type A (Low resistance)
  - Type B (High CC capacity)
  - Type C (High capacity and efficiency)
- HEV
  - Fully-Charged method
- PHEV
- EV or Consumer

KURANODE™

< 4 methodologies we have tested >
1: Smaller particle size
2: New purification method
3: "Fully-charged method"
4: "Alkali impregnation method"

< Using Type2 as an anode material
< Using Test product C as an anode material

Today's main topics

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Structure and Features of HC

Graphite

Theoretical Capacity
~372 mAh/g

➢ Hard carbon has cavities that are able to store more Li as cluster-like Li.
➢ Because of plant-derived structures, KURANODE™ has a lot of cavities.
For enhancing capacity

Charge condition (Li for counter electrode)
- Step 1: (CC) 0.2C
- Step 2: (CV) 0V, 0.02mA-cut

3 Utilizing un-inserted cavities (Electrochemically)
4 Increasing cavities (To use chemical reaction)

Graphite

Voltage (V vs Li/Li⁺)

Capacity (mAh/g)

KURANODE™

Utilizing un-inserted cavities (Electrochemically)
Increasing cavities (To use chemical reaction)
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What is ‘Fully-Charged method’?

Anode material: KURANODE™ Type2
Anode composition: Type2/PVDF=94/6 (w/w), Thickness ~80μm
Counter electrode: Li metal (Half Cell)

Utilizing un-inserted cavities (Electrochemically)

<table>
<thead>
<tr>
<th>Line</th>
<th>Charging Condition</th>
<th>Charge Capacity [mAh/g]</th>
<th>Discharge Capacity [mAh/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1. CC(0.2C) → 2. CV (0V, 0.02mA)</td>
<td>380</td>
<td>332</td>
</tr>
<tr>
<td>B</td>
<td>1. CC(0.2C) → 2. CV (0V, ~500 mAh/g)</td>
<td>500</td>
<td>440</td>
</tr>
<tr>
<td>C</td>
<td>1. CC(0.2C) → 2. CV (0V, ~600 mAh/g)</td>
<td>600</td>
<td>526</td>
</tr>
</tbody>
</table>
Li-NMR results of HC anodes*

\(^7\text{Li} \text{MAS-NMR} \,(\text{@303K})

- No peak derived from Li metal
- A lower magnetic field shift peak derived from Li clusters

<table>
<thead>
<tr>
<th>Chemical shift / ppm</th>
<th>KURANODE\textsuperscript{TM} Type 2</th>
<th>Other hard carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>~140ppm</td>
<td><img src="image1.png" alt="Graph" /></td>
<td>~106ppm</td>
</tr>
</tbody>
</table>

*\text{~500 mAh/g charged}

Features of KURANODE\textsuperscript{TM}

Many cavities exist! (Because of plant-derived structures)
**Cell structure of full cell [laminate type cell]**

We provided full cells under the following conditions to check the rate and temperature characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Cathode</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Active materials</strong></td>
<td>NCM (111)</td>
<td>KURANODE™ Type2</td>
</tr>
<tr>
<td><strong>Specific capacity (Charge)</strong></td>
<td>175 mAh/g</td>
<td>I. 400, II. 500, III. 600 mAh/g</td>
</tr>
<tr>
<td><strong>Compositional ratio (weight)</strong></td>
<td>NCM 100</td>
<td>HC 100</td>
</tr>
<tr>
<td></td>
<td>AB 3</td>
<td>PVdF 6.4</td>
</tr>
<tr>
<td></td>
<td>Graphite 3</td>
<td>PVdF 6.4</td>
</tr>
<tr>
<td></td>
<td>PVdF 3</td>
<td>PVdF 6.4</td>
</tr>
<tr>
<td><strong>Coating weight</strong></td>
<td>one surface 11.9 mg/cm²</td>
<td>I. 5.1, II. 4.1, III. 3.4 mg/cm²</td>
</tr>
<tr>
<td></td>
<td>both surfaces 23.8 mg/cm²</td>
<td>I. 10.2, II. 8.1, III. 6.8 mg/cm²</td>
</tr>
<tr>
<td><strong>Capacity ratio</strong></td>
<td></td>
<td>Anode / Cathode = 1.0</td>
</tr>
</tbody>
</table>

We controlled the design capacity of the cells (I. 400, II. 500, III. 600 mAh/g) by controlling the coating weight of anode materials.
All KURANODE™ Type2 superior to graphite in charge/discharge rate characteristics.
Specifically, ~500 mAh/g charged KURANODE™ Type2 was good characteristics.

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Capacity retention factor vs ambient temperature

Charge/Discharge condition (CC)
Charging : 300 mA (ca. 1/3C) to 4.2 V at 25°C
Discharging : 300 mA (ca. 1/3C) to 2.0 V/3.0 V (KURANODE/Graphite) at each temp. as shown in the graph

Charge/Discharge condition (CC)
Charging : 300 mA (ca. 1/3C) to 4.2 V at each temp. as shown in the graph
Discharging : 300 mA (ca. 1/3C) to 2.0 V/3.0 V at 25°C (KURANODE/Graphite)

All KURANODE™ Type2 superior to graphite in temperature characteristics.

“Fully-charged method” leads to increasing capacity with keeping HC features!!

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What is ‘Alkali Impregnation method’?

Main purposes

- Increasing “Cavity” by alkali activation
- Making the new bonds between carbon crystals
- Controlling heat shrinkage by the new bonds and maintaining cavities
Preparation method

Coconuts Shell

Carbonization
~600°C

Charcoal

Grinding
using ball milling

Charcoal Powder

Alkali Impregnation

Heat Treatment and Purification
under HCl/N₂ Atmosphere
~1200°C

Hard Carbon

CVD Treatment
under Hydrocarbon/N₂ Atmosphere
~800°C

Immerging Charcoal in aqueous Alkali and drying up
Initial charge/discharge properties

```
<table>
<thead>
<tr>
<th>Sample</th>
<th>True density g/cc</th>
<th>Expansion ratio at lithiation</th>
<th>Discharge Capacity mAh/g</th>
<th>Discharge Capacity mAh/cc a)</th>
<th>Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref) Graphite</td>
<td>2.2</td>
<td>~1.1</td>
<td>377</td>
<td>754</td>
<td>93.0</td>
</tr>
<tr>
<td>Alkali add. + CVD</td>
<td>1.43</td>
<td>~1</td>
<td>531</td>
<td>759</td>
<td>91.7</td>
</tr>
<tr>
<td>Alkali add.</td>
<td>1.46</td>
<td>~1</td>
<td>484</td>
<td>595</td>
<td>87.8</td>
</tr>
<tr>
<td>Ref) Just Heating</td>
<td>1.48</td>
<td>~1</td>
<td>450</td>
<td>553</td>
<td>84.2</td>
</tr>
</tbody>
</table>
```

➢ “Alkali add. + CVD” shows very high discharge capacity per vol. on par with it of graphite!

a) Capacity per vol = Capacity per weight * True density / expansion ratio
Pore Structure and Moisture absorbency

Covering with thermolysis product by CVD results in
- reducing SSA
- reducing amount of Oxygen

Low moisture absorbency!

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water Content a) ppm</th>
<th>SSA m²/g</th>
<th>O wt%</th>
<th>H wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali add. + CVD</td>
<td>221</td>
<td>2.5</td>
<td>0.29</td>
<td>0.13</td>
</tr>
<tr>
<td>Alkali add.</td>
<td>31500</td>
<td>34</td>
<td>0.61</td>
<td>0.08</td>
</tr>
<tr>
<td>Ref) Just Heating</td>
<td>52200</td>
<td>28</td>
<td>0.67</td>
<td>0.10</td>
</tr>
</tbody>
</table>

a) at 170 hr

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How about “Alkali impregnation” + “Fully-Charged”?  

Much the same properties with or without “Fully-charged method”

- a limit of the amount of cavities
- just making cavities utilisable.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Discharge Capacity</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mAh/g</td>
<td>mAh/cc a)</td>
</tr>
<tr>
<td>Alkali add. + CVD_600mAh/g</td>
<td>537</td>
<td>767</td>
</tr>
<tr>
<td>Ref) NaOH add. + CVD</td>
<td>531</td>
<td>759</td>
</tr>
</tbody>
</table>
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We have enhanced the capacity of HC by two methods:

1. “Fully-charged method” - Electrochemical method
   - increasing capacity with keeping HC features (rate and temperature characteristics)

2. “Alkali impregnation method” - Using Chemical reaction method
   - 531 mAh/g [759 mAh/cc], higher capacity than graphite
   - low moisture absorbency

→ Suitable for xEV applications
Company Introduction ~Battery Materials Research Lab~

Function of Battery Materials Research Lab. in Kurashiki R&D Center

➢ R&D on battery related materials
➢ Testing of battery & battery materials
   ✓ Electrochemical Properties
   ✓ Chemistry, Recipe

Active Materials

1. Binder
   - Water base binder for LiFe (O)
   - Water base binder for NaIB (O)
   - New water base Binder (R)

2. Electrolyte
   - Gel electrolyte (R)

3. Additives
   - Conductive Additives (K)

4. Separator
   - Vinyl Paper for Alkaline Primary Battery (C)
   - New Type Separator for LIB (K)

5. Carbon for LiN, NaIB and LiIC (C)
   - Activated Carbon for LiC, LiS and EDLC (C)
   - Organic Cathode for LiFe (C)
   (C): Commercialized
   (D): Under Development
   (R): Research

Kurashiki R&D Center
Increasing cavities
(To use chemical reaction)

correlate with edge direction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Discharge Capacity</th>
<th>True density (BuOH)</th>
<th>True density (He)</th>
<th>Raman spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mAh/g</td>
<td>g/cc</td>
<td>g/cc</td>
<td>Half maximum full-width of D-band cm⁻¹</td>
</tr>
<tr>
<td>Alkali add. + CVD</td>
<td>531</td>
<td>1.43</td>
<td>1.41</td>
<td>259</td>
</tr>
<tr>
<td>Alkali add.</td>
<td>484</td>
<td>1.46</td>
<td>2.05</td>
<td>213</td>
</tr>
<tr>
<td>Ref) Just Heating</td>
<td>450</td>
<td>1.48</td>
<td>2.08</td>
<td>204</td>
</tr>
<tr>
<td>電池設計</td>
<td>充電 (mAh)</td>
<td>放電 (mAh)</td>
<td>效率</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Bio②</td>
<td>400mAh/g</td>
<td>911</td>
<td>910</td>
<td>99.9%</td>
</tr>
<tr>
<td></td>
<td>500mAh/g</td>
<td>929</td>
<td>929</td>
<td>100.0%</td>
</tr>
<tr>
<td></td>
<td>600mAh/g</td>
<td>929</td>
<td>927</td>
<td>99.8%</td>
</tr>
<tr>
<td>黑鉛</td>
<td>360mAh/g</td>
<td>1015</td>
<td>1002</td>
<td>98.7%</td>
</tr>
</tbody>
</table>

[Bio-HC]
Charge: 270mA, cc 4.2V cut-off at 25 ℃
Discharge: 270mA, cc 2.0V cut-off at 25 ℃

[黑鉛]
Charge: 330mA, cc 4.2V cut-off at 25 ℃
Discharge: 330mA, cc 3.0V cut-off at 25 ℃