Effects of Surface Chemistry of Carbon on Hydrogen Evolution Reaction in Lead Carbon Electrodes

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Carbon in Negative Plates
Pronounced H₂ Evolution

H₂ Overpotential

Electrocatalytic Activity

Pb → PbSO₄

Potential vs. NHE

2H⁺ + 2e⁻ → H₂

PbSO₄ → Pb

Current

✓ Surface area

✓ Surface active sites

2. A. Allouche, et al., Carbon, 44 (2006) 3320-3327

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Electrocatalytic Activity of Pure Carbons

Motivation

Carbon
- Surface chemistry
- Specific surface area

Mechanism
- Electrocatalytic activity
- Double layer capacity

Performance
- Dynamic charge acceptance
- Gassing

→ No simple correlation with physical properties
Outline

MATERIAL
Functionalized Carbon Materials

MECHANISM
Electrocatalytic Activity of Pure Carbons

PERFORMANCE
Electrochemical Activity of Negative Electrodes
Functionalyzed Carbon Materials

Chemical Treatment

Direct synthesis
Wet chemical treatment
Gas phase treatment

Possible effects:
- Polarity
- pH
- Adsorption capability
- Conductivity
- Porosity
- .....
Functionalized Carbon Materials

XPS – Surface Functionality

- Presence of oxygen groups in original AC

- Incorporation of nitrogen groups by chemical treatment

- Amount of surface functionality:
  - AC-N2
  - AC-N1
  - AC-30
  - AC
Functionalized Carbon Materials

N₂ Sorption – Surface Area

- Original AC and AC-30 mainly consist of micropores
- Decrease in surface area by chemical treatment
- Significant low BET of AC-N1 and AC-N2 due to the blocked / filled micropores

![Graphs showing nitrogen sorption on different types of carbon materials](image-url)
Functionalized Carbon Materials

Summary

- Activated carbons with different amount of functional groups
- Porosity decrease by the modification of activated carbon
- Higher surface functionality resulted in lower BET surface area

<table>
<thead>
<tr>
<th></th>
<th>AC</th>
<th>AC-30</th>
<th>AC-N1</th>
<th>AC-N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon [%]</td>
<td>95</td>
<td>89</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>Nitrogen [%]</td>
<td>0.4</td>
<td>6.7</td>
<td>14</td>
<td>23</td>
</tr>
<tr>
<td>Oxygen [%]</td>
<td>4.6</td>
<td>4.3</td>
<td>11</td>
<td>17</td>
</tr>
<tr>
<td>$S_{BET}$ [m$^2$/g]</td>
<td>1700</td>
<td>1100</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>$S_{micro}$ [m$^2$/g]</td>
<td>1450</td>
<td>950</td>
<td>-</td>
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Electrocatalytic Activity of Pure Carbons

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Electrocatalytic Activity of Pure Carbons
Rotating Disk Electrode Measurements

- Working electrode: Glassy Carbon
  - Drop casting of carbon from aqueous dispersion
  - 0.2 cm² apparent surface area
- Counter electrode: Platinum
- Reference electrode: RHE
- Electrolyte: 1M H₂SO₄ (de-aerated)
Electrocatalytic Activity of Pure Carbons
Cyclic Voltammetry – Hydrogen Evolution

- $\text{H}_2$ evolution overpotentials: AC-N2 > AC-N1 > AC-30 > AC
- Increased surface treatment led to lower activity towards $\text{H}_2$ evolution
Electrocatalytic Activity of Pure Carbons
Cyclic Voltammetry – Double Layer

- Similar capacitance of AC, AC-N1 and AC-N2 → Surface chemistry as important as BET
- Higher capacitance of AC-30 due to the presence of nitrogen groups
Electrocatalytic Activity of Pure Carbons

Summary

- Lower activity of carbon towards H₂ evolution by higher nitrogen content
- Increased double layer capacitance by higher nitrogen content
Electrocatalytic Activity of Pure Carbons

Motivation

Carbon
- Surface chemistry
- Specific surface area

Mechanism
- Electrocatalytic activity
- Double layer capacity

Performance
- Dynamic charge acceptance
- Gassing
Electrochemical Activity of Negative Electrodes

Electrode Pasting and Cell Assembly

- 2V laboratory cells
  - Enhanced flooded batteries (EFB)
  - 2 positive, 1 negative electrode
  - Carbon additives: AC, AC-30 and AC-N1
  - 1 Ah capacity
- Manual pasting of electrodes
- Cell assembly
- Container formation

2V Test-cell
Electrochemical Activity of Negative Electrodes
Cyclic Voltammetry – Hydrogen Evolution

- Different activity of negative electrodes towards H₂ evolution: AC > AC-30 > AC-N1
- Similar observation obtained from the cyclic voltammetry of pure carbons
Electrochemical Activity of Negative Electrodes

Cyclic Voltammetry – Double Layer

- Double layer capacitance of negative electrodes: AC-30 ~ AC > AC-N1
- No direct correlation between the capacitance of lead-carbon plates and pure carbons
Electrochemical Activity of Negative Electrodes

Charge Acceptance

- Charge acceptance of negative electrodes: AC-30 ~ AC > AC-N1
- Despite the low BET, high charging currents of AC-N1

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Electrochemical Activity of Negative Electrodes

Summary

- Lower activity of carbon in terms of H₂ evolution by higher nitrogen doping
- High charge acceptance of negative electrodes even with a very low BET carbon

![Graph showing current vs potential and BET values](image)

- **BET [m²/g]**
  - AC: 1700
  - AC-30: 1100
  - AC-N1: 20

- **N [%]**
  - AC: 0.4
  - AC-30: 6.7
  - AC-N1: 14

- **After discharge 90% SoC**
  - AC: 1.0
  - AC-30: 0.8
  - AC-N1: 0.5
Electrocatalytic Activity of Pure Carbons

Conclusion

Carbon
- Surface chemistry
- Specific surface area

Optimized carbon additive by sufficient nitrogen content and porosity

Mechanism
- Electrocatalytic activity
- Double layer capacity

Performance
- Dynamic charge acceptance
- Gassing
Thank you for your attention!

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