CARBON CONDUCTIVE ADDITIVES FOR ELECTRODES IN ELECTROCHEMICAL ENERGY STORAGE DEVICES

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CARBON CONDUCTIVE ADDITIVES FOR ELECTRODES IN ELECTROCHEMICAL ENERGY STORAGE DEVICES

Introduction on carbon conductive additives

Conductive additives in symmetric supercapacitors

Current collector coating in Li-ion positive electrodes
Conductive carbon black structure

Carbon black aggregates of primary particles

Carbon black structure:
Total accessible void volume per unit weight of carbon black

- Intra-aggregate space
- Interstices between the aggregates
- Primary particle porosity

Transmission electron microscopy

Absorption stiffness (oil absorption)

<table>
<thead>
<tr>
<th>Product</th>
<th>Absorption Stiffness (mL/5g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NERGY® SUPER C45</td>
<td>37</td>
</tr>
<tr>
<td>NERGY® SUPER C65</td>
<td>32</td>
</tr>
</tbody>
</table>
Conductive carbon black structure

Primary particle size

Carbon black structure:
Total accessible void volume per unit weight of carbon black

- Intra-aggregate space
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Transmission electron microscopy

Absorption stiffness (oil absorption)

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Current collector coating in Li-ion positive electrodes
Effect of conductive additives on the volume resistivity of activated carbon – conductive additive mixtures

Carbon black (Super C45, Ensaco 350P) and graphite (KS 6L) conductive additives reduce the volume resistivity of activated carbon mixtures.
The press density of activated carbon – conductive additive mixtures increases with increasing additive amount.

- Graphite typically improves the compressibility of powder mixtures.
- Carbon black aggregates might fill the voids between activated carbon particles.
Expected impact of conductive additives on the specific surface area of activated carbon electrodes

- Low surface area conductive additives are expected to lower the surface area of activated carbon electrodes.
- The surface area of Ensaco 350P is comparable to the one of the activated carbon.
Activated carbon mixtures containing carbon black (Super C45, Ensaco 350P) conductive additives require large amounts of solvent to be processed.

The effect is negligible when small amounts of low surface area carbon black (e.g. 5 wt.% of Super C45) are used.

Solvent:
\( \text{H}_2\text{O:alcohol} \)

1:1 (wt.)
Electrode preparation, cell assembly and testing

Electrode composition:
- 10 wt.% binder (PTFE)
- 90 wt.% carbon material
- activated carbon: conductive additive => 95:5 (wt.)
- rolled and pressed
- freestanding electrodes (no current collector)
- electrode area: 1.13 cm\(^2\), thickness ~ 200 µm
- loading (C): ~ 24 mg cm\(^{-2}\), density (C) ~ 0.6 g cm\(^{-3}\)

Cell assembly:
- 2 identical electrodes, symmetric configuration
- 1 mol dm\(^{-3}\) tetraethylammonium tetrafluoroborate in acetonitrile

Testing:
- impedance spectroscopy, cyclic voltammetry
- CV with increasing sweep rate for rate capability evaluation
Effect of conductive additives on the impedance spectra of symmetric supercapacitors

The addition of carbon black (Super C45, Ensaco 350P) results in lower impedance compared to a cell made with pure activated carbon electrodes.

Graphite (KS 6L) has a minor impact on the impedance.

<table>
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<th>Additive</th>
<th>ESR [Ohm]</th>
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<tbody>
<tr>
<td>5 wt.% E350P</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>5 wt.% SC45</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>5 wt.% KS 6L</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Pure AC</td>
<td>1.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Effect of conductive additives on the capacitance of symmetric supercapacitors

The addition of Ensaco 350P does not affect the gravimetric capacitance at low sweep rate and improves it at high rates.
Effect of conductive additives on the rate capability of symmetric supercapacitors

At low sweep rate the gravimetric capacitance of the cells is dominated by the total surface area of the electrodes, while at high rates other parameters, like the pore structure and resistivity of the electrode, seem to play a more important role.

This transition takes place at higher rates when the volumetric capacitance is considered.

The polar surface of Super C45 may improve the wettability of the electrodes.
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Current collector coating in Li-ion positive electrodes
C-NERGY™ Li-Quid 101: ready-to-use water based dispersion for current collector coating

- Ready-to-use water based dispersion of very fine carbon powder, may be applied by coating or printing.
The adhesion decreases when large amounts of conductive additive are used.

Thank to its lower surface area, graphite helps preventing adhesion loss.

Adhesion is enhanced by a thin layer of Li-Quid 101 primer.
Effect of current collector coating on the performance of NMC positive electrodes in Li half-cells

CC-CV 3 – 4.3 V vs Li/Li⁺, 1 M LiPF₆ in EC:EMC (1:3 v/v), 2 wt.% SC65

- The thin C-NERGY™ Li-Quid 101 layer helps preventing the increase of electrode polarisation during cycling; consequently the cycling stability improves significantly.
Effect of current collector coating on the performance of NMC positive electrodes in Li half-cells

CC-CV 3 – 4.3 V vs Li/Li\textsuperscript{+}, 1 M LiPF\textsubscript{6} in EC:EMC (1:3 v/v), 2 wt.% SC65

- The thin C-NERGY\textsuperscript{TM} Li-Quid 101 layer helps preventing the increase of electrode polarisation at high rates, resulting in improved galvanostatic charging up to 1 C rate in NMC electrodes containing a low amount of conductive additive.
Conclusions

- Conductive additives improve the conductivity of porous electrodes, but can also be used to tailor their porous structure; the high rate performance of symmetric supercapacitors can be improved by the addition of carbon black or graphite conductive additives.

- C-NERGY™ Li-Quid 101 improves the adhesion and the electrical contact between the metal foil and the electrode mass; this leads to lower internal electrical resistance, improves performance in the high current drain regime and extends cell life.

- The amount and type of conductive additive play an important role in the adhesion of Li-ion positive electrodes.
Acknowledgments

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Thank you for your attention