Synthesis of hybrid lamellar silica and study of their dispersion in a poly(ethylene oxide) matrix.

Gilles TOUSSAINT

Introduction

Lithium batteries

Laptops
Cell phones

Electric Vehicles

Storage of renewable energy

Electrolyte
Introduction

Solid polymer electrolytes
Poly(ethylene oxide) «PEO»

**Advantages**
- Light weight
- Designing
- Stability vs Li^0
- Mechanical stability

Mechanical reinforcement

**Particle effects in «PEO» electrolytes**

- Conductivity *
- Interfacial resistance with Li^0**

** W. Krawiec et al, J. Power Sources (1995) 54, 310

Introduction

Lamellar fillers

Lamellar fillers: ~ 1 nm
20 nm → µm

Nanoﬁllers with high aspect ratio & specific surface for individual sheets

**Drawbacks:** aggregation in tactoids

Periodicity d_{001}
Tactoid (= aggregate)
Agglomerate of tactoids ~ µm
Introduction

Nanocomposites: lamellar fillers

- Intercalated
- Exfoliated
- Phase separated

Compatibilization In-situ polymerization

Organic:
- Ammonium salt: $R_4N^+Cl^-$
- Silane $R-Si-X_3$

$\Delta d_{001}$

Compatabilization
In-situ polymerization
Objective

Objective:
- Synthesize hybrid lamellar silica compatibilized towards PEO
- Study of the dispersion of the hybrid lamellar silica in PEO electrolytes

Outlook

- Introduction
- Synthesis of hybrid lamellar silica:
  - Principles
  - Composition, Morphology
  - Porosity
  - Applications
- Conclusions and perspectives
Outlook

- Introduction

- **Synthesis of hybrid lamellar silica:**
  - Principles
  - Composition, Morphology
  - Porosity
  - Applications

- Conclusions and perspectives

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**Synthesis of hybrid lamellar silica**

*Liquid Crystal Templating: silica synthesis*

\[
H_2O \xrightarrow{} n \text{Si(OCH}_2\text{CH}_3)_4 + n \text{CH}_3\text{CH}_2\text{OH}
\]

Synthesis of hybrid lamellar silica

Silanization: organomodification

Silane coupling agent:

Hydrolyzable group (Cl, OCH₃, ...)

Grafting to silica surface:

Compatibilization to PEO matrix

Polymer matrix = PEO:

Silane agents:

Synthesis of hybrid lamellar silica compatibilized towards the PEO matrix in 2 steps
1) Liquid Crystal Templating: silica synthesis

2) Template extraction & silanization: organomodification

Introduction

Synthesis of hybrid lamellar silica:
- Principles
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Conclusions and perspectives

1) Liquid Crystal Templating: silica synthesis

Composition, morphology of lamellar silica

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As-synth silica

TGA - DSC

XRD

\[ d_{101} = 40 \text{ Å} \]

Composition, morphology of lamellar silica

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2) Template extraction & silanization: organo-modification

« As-Synth » silica

GPTMS:

PEOTMS:

Si NMR

As-synth

GPM

PEO

→ Covalent grafting of silane

→ Grafting less effective than GPM

Size PEO-TMS > GPTMS

* B. Zhao, Progress in Polymer Science (2000 25, 677-710)

Composition, morphology of lamellar silica

XRD

24 Å

Periodicity

20 Å

Grafting density

d_{001} ↔ grafting density
Composition, morphology of lamellar silica

2) Template extraction & silanization: organo-modification

- **GPM**: Hybrid silica
  - GPTMS + Propan-2-ol
- **PEO**: Hybrid silica
  - PEOTMS + Propan-2-ol
- **Surf Free**: silica
  - Propan-2-ol
Lamellar silica: specific surface & porosity

H3: plate-like particles

H4: Narrow-slit like pores

N₂ adsorption:

- Surf-Free
- GPM
- PEO
- As-synth

All isotherms = Type IV (hysteresis) → Mesopores
Lamellar silica: specific surface & porosity

Pore size distribution

Summary of nitrogen adsorption analyses:

<table>
<thead>
<tr>
<th></th>
<th>As-Synth</th>
<th>PEO</th>
<th>GPM</th>
<th>Surf-Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotherm type</td>
<td>Meso</td>
<td>Meso</td>
<td>Meso</td>
<td>Meso</td>
</tr>
<tr>
<td>Hysteresis type</td>
<td>IV: plate-like</td>
<td>III: narrow-slit like</td>
<td>III: narrow-slit like</td>
<td>III: narrow-slit like</td>
</tr>
<tr>
<td>(BET S_0 , (m^2/g))</td>
<td>8,5</td>
<td>122,9</td>
<td>375,4</td>
<td>612,3</td>
</tr>
<tr>
<td>V − t :</td>
<td>Non porous</td>
<td>Micro</td>
<td>Micro</td>
<td>Micro</td>
</tr>
<tr>
<td>Comparison BJH – BET:</td>
<td>Meso</td>
<td>Meso</td>
<td>Micro</td>
<td>Micro</td>
</tr>
<tr>
<td>Micropore surface area ((m^2/g)):</td>
<td>(/)</td>
<td>28,6</td>
<td>236,9</td>
<td>376,2</td>
</tr>
<tr>
<td>Pore distribution</td>
<td>Pores &lt; [8-9] nm</td>
<td>Pores &lt; 4 nm</td>
<td>Pores &lt; 4 nm</td>
<td>Pores &lt; 4 nm</td>
</tr>
<tr>
<td>Silanechain size</td>
<td>(/)</td>
<td></td>
<td></td>
<td>(/)</td>
</tr>
</tbody>
</table>
As Synth: Specific surface measured = external surface of «Plate-like particles» (tactoids)

After silanization: measure of «Narrow-slit like mesopores» and micropores inside the platelets

=> silane covers the micropores => if silane size ↑, quantity of micropores measured ↓

Applications

- **Dispersion in solution (propan-2-ol)**

  As-synth  
  PEO-silica

- **Dispersion in PEO**
  (Mw ~ 6000 g/mol)

  Rheology analysis:

  Percolation threshold for silica concentration < 1 wt %
Outlook

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Conclusions and perspectives

- Synthesized different hybrid lamellar silicas:

Conclusions and perspectives

- High specific surface
  - Mesopore ∈ [2, 4] nm
  - Micropores
- Interesting lamellar fillers

G. Toussaint, M. A. Rodriguez, R. Cloots, J. Rubio, F. Rubio, B. Vertruyen, C. Henrist,

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Conclusions and perspectives

- If no complete exfoliation indicated by others analyses, it is important to determine the rheological percolation in effective volume fraction of tactoids
  - comparison with theoretical threshold = good indication of exfoliation

- Lamellar fillers are more interesting than nanospheres only with significant exfoliation
- Better dispersion of lamellar silica in low molecular weight PEO

G. Toussaint, R.Cardinaels, C. Ozdilek, P. Moldenaers, M. Alexandre, C. Henrist, R.Cloots
*Macromolecules* (Submitted)
Conclusions and perspectives

**Perspectives:**

- **In-situ polymerization** of ethylene oxide from GPM-type silica
- Complete study of **particle effect on electrochemical properties** related to their dispersion
- Relate the dispersion of hybrid lamellar silica with the surface properties of particles by **inverse gas chromatography** → prediction of dispersion according to interaction of silica surface to their environment

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Thank you for your attention