Electrochemical Impedance Spectroscopy: Understanding the Role of the Reference Electrode

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**Aim**

Design a reference electrode (RE) stable in organic electrolytes with a potential positive to that of the solid electrolyte interphase (SEI) formation to substitute metallic lithium and obtain accurate impedance spectra using three-electrode cells.

**Experimental**

- Bi pieces lithiated in two-electrode cells at C/10, EC/DMC 1:1, 1M LiPF₆.
- Linear polarization ±50 mV vs. OCP.

**Reference electrode preparation**

Electrochemical lithiation (in situ preparation):

- The alloy consists of a mixture of LiBi, Li₂Bi and Li₃Bi phases (XRD).

**Reference electrode stability**

- Stable potential due to two lithiated phases equilibrium.
- Li₃Bi unsuitable: potential negative to the SEI formation.

**Long-term stability**

<table>
<thead>
<tr>
<th>Potential [V] vs. Li⁺/Li⁺</th>
<th>Alloy</th>
<th>Lithiation after charge</th>
<th>After LP (2°)</th>
<th>1 week</th>
<th>3 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBi₄</td>
<td>0.804</td>
<td>0.854</td>
<td>0.828</td>
<td>0.829</td>
<td></td>
</tr>
<tr>
<td>LiBi</td>
<td>0.805</td>
<td>0.855</td>
<td>0.828</td>
<td>0.831</td>
<td></td>
</tr>
<tr>
<td>Li₃Bi</td>
<td>0.808</td>
<td>0.858</td>
<td>0.805</td>
<td>0.810</td>
<td></td>
</tr>
<tr>
<td>Li₂Bi BM</td>
<td>0.808</td>
<td>0.855</td>
<td>0.810</td>
<td>0.810</td>
<td></td>
</tr>
</tbody>
</table>

* Linear Polarization

**Polarization behaviour**

- Li₃Bi electrodes exchanged much higher current than Li. Small parasitic current flowing through the Li₃Bi RE will not change its potential.
- Hysteresis measured for the reference electrodes from CV.

**Impedance spectra**

- Li₃Bi RE gives comparable results to Li RE in GEIS (LCO WE).

**Conclusions**

- Li-Bi alloys prepared by in situ methods are suitable as RE.
- Li₃Bi RE exhibits a more stable potential than Li upon a current flow.
- Li₃Bi RE gives comparable results to Li RE in Galvano-electrochemical impedance spectroscopy.

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