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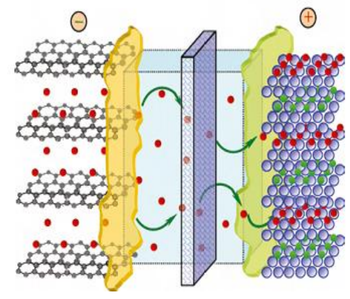

Electrochemical Impedance Spectroscopy: Understanding the Role of the Reference Electrode

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Aim

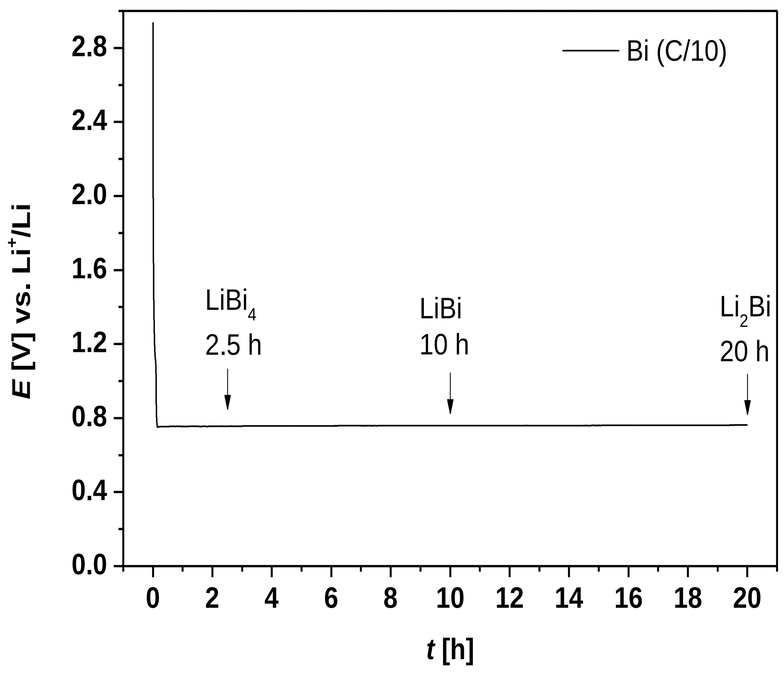
Design a reference electrode (RE) stable in organic electrolytes with a potential positive to that of the solid electrolyte interphase (SEI) formation to substitute metallic lithium and obtain accurate impedance spectra using three-electrode cells.

Experimental

- Bi pieces lithiated in two-electrode cells at C/10. EC/DMC 1:1, 1M $LiPF_6$.
- Linear polarization ±50 mV vs. OCP.

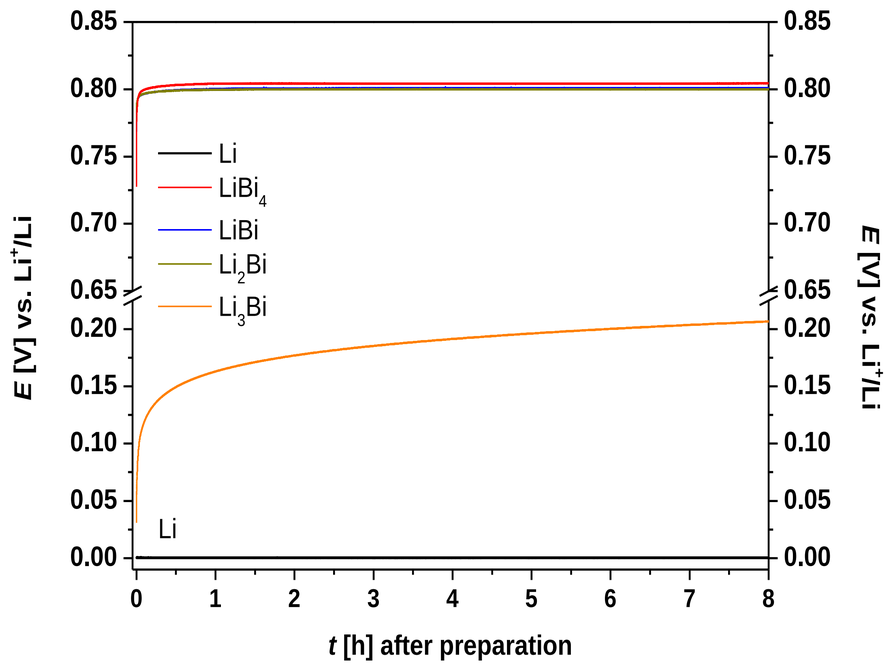
Reference electrode preparation

Electrochemical lithiation (*in situ* preparation):



- The alloy consists of a mixture of LiBi, Li_2Bi and Li_3Bi phases (XRD).

Reference electrode stability



- Stable potential due to **two lithiated phases equilibrium.**
- Li_3Bi unsuitable: potential negative to the SEI formation.

Long-term stability

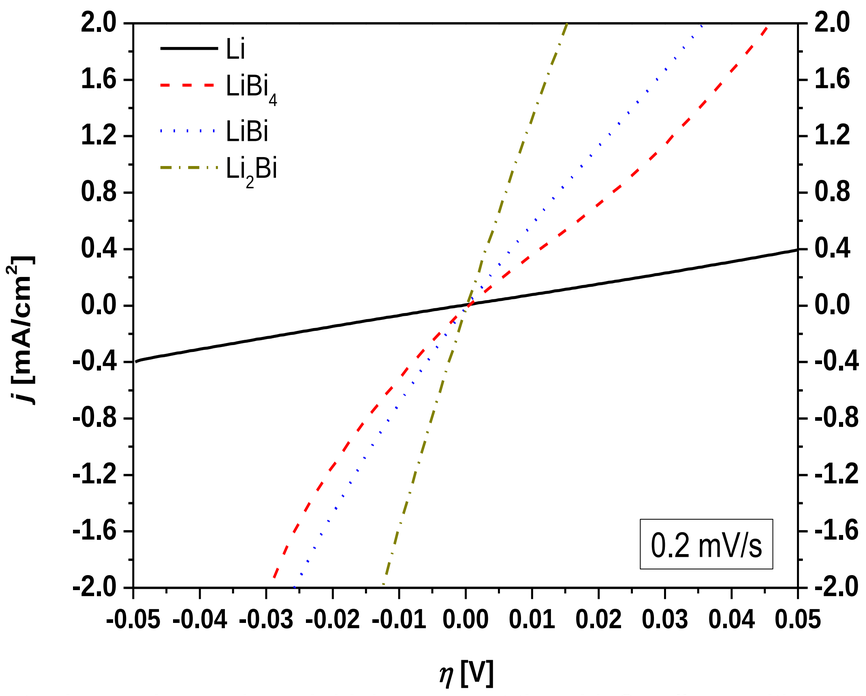
Potential [V] vs. Li^+/Li:

- Stable potentials after preparation

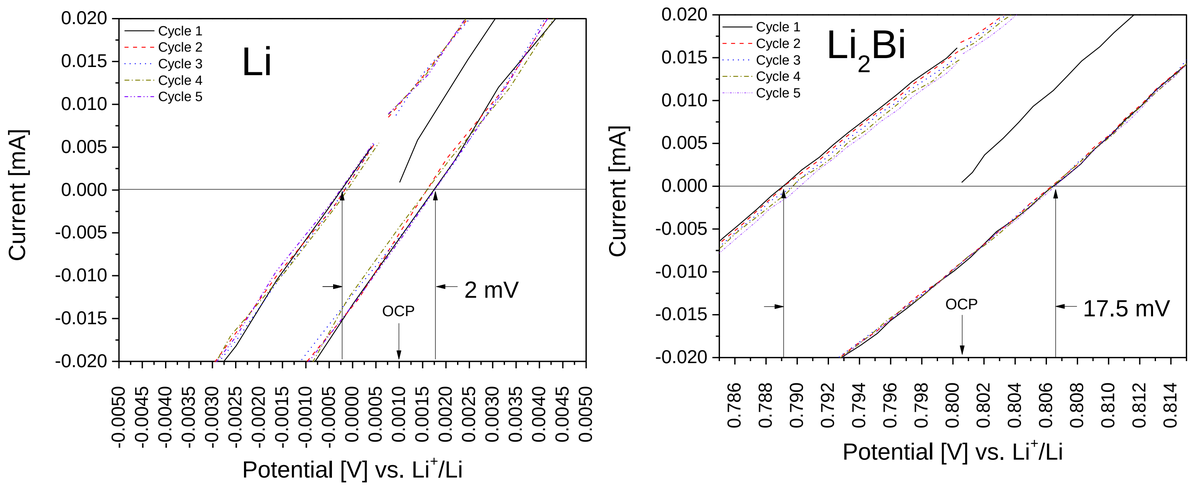
* Linear Polarization

Alloy	8h after charge	After LP (*)	1 week	3 weeks
$LiBi_4$	0.804	0.854	0.828	0.829
LiBi	0.805	0.855	0.828	0.831
Li_2Bi	0.808	0.858	0.805	0.810
Li_2Bi BM	0.808	0.858	0.810	0.810

Polarization behaviour

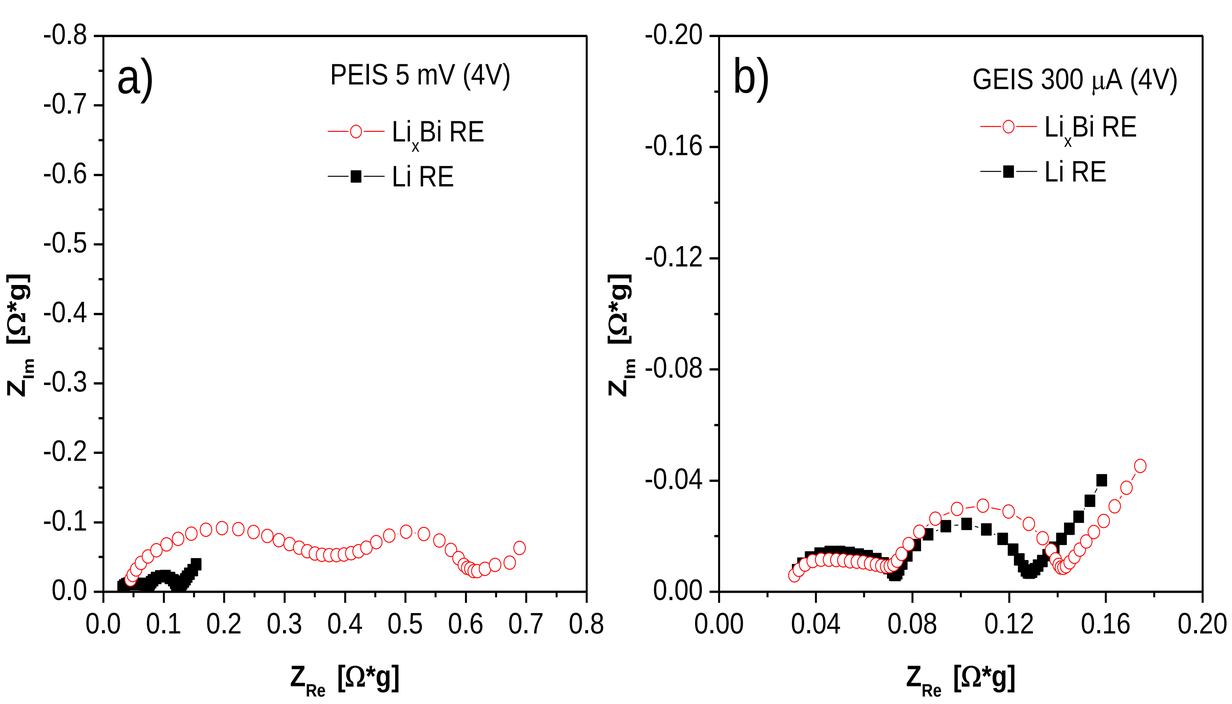


- Li_xBi electrodes exchanged much higher current than Li. Small parasitic current flowing through the Li_xBi RE will not change its potential.



- Hysteresis measured for the reference electrodes from CV

Impedance spectra



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

Conclusions

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

Acknowledgments: The authors express their gratitude to the members of the Battery Group at PSI for the experimental support and advice and to TIMCAL SA (Bodio, Switzerland) for financial support.