Surface Analysis of Pre-Lithiated Electrodes by Means of Glow Discharge-Sector Field-Mass Spectrometry (GD-SF-MS)

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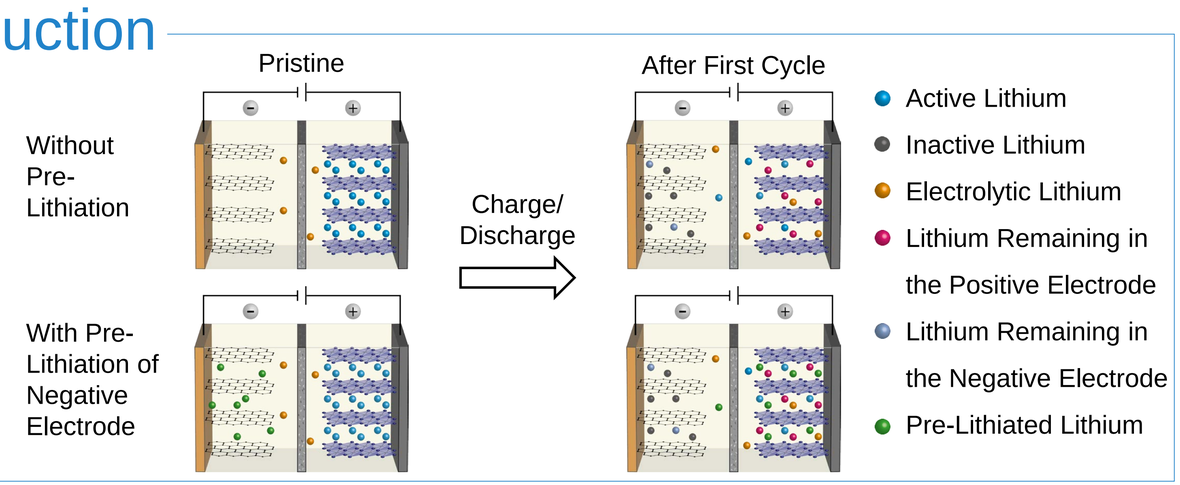
Introduction

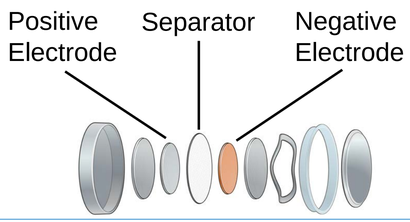
- Lithium ion batteries (LIBs), the most commonly used rechargeable energy storage system nowadays, suffer from decreased lifetime caused by aging [1, 2]
- Active lithium loss (ALL) in the first charge/discharge cycle lead to capacity fading of LIBs
- Pre-lithiation describes the addition of supplementary lithium to one of the electrodes, prior to cell operation and is used to compensate ALL[3]
- Exploration of the lithium distribution and concentration in carbonaceous electrodes, pre-lithiated with different techniques, to gain a deeper understanding



Methods

Cell Chemistry

- In-house produced electrodes with 95% SG3 Graphite, 0.5% conductive carbon (SuperC), 4.5% binder (3% carboxymethyl cellulose, 1.5% styrene-butadiene rubber)
- LIB cells with a carbonaceous negative electrode, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ positive electrode, polypropylene separator and 40 µL electrolyte (1 mol L^{-1} $LiPF_6$, mixture of ethylene carbonate and ethyl methyl carbonate (30/70 wt%))



Parameters of GD-SF-MS

Thermo Scientific Element GD Plus	
Parameter	**Value**
Discharge Voltage / V	1000
Discharge Current / mA	8.00
Pulse Duration / µs	10
Pulse Frequency / kHz	4
Duty Cycle / %	4.0
Gas Flow Discharge Gas (Ar) / mL min^{-1}	450

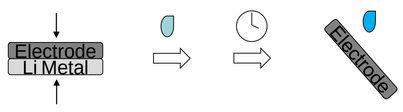
Sample Digestion and ICP-OES Parameters

- Microwave assisted acid digestion for ICP-OES

Spectro ARCOS ICP-OES	
Parameter	**Value**
RF Power / W	1400
Cooling Gas (Ar) / L min^{-1}	12.0
Sample Gas (Ar) / L min^{-1}	0.85
Auxiliary Gas (Ar) / L min^{-1}	0.80
Nebulizer	Cross Flow
Torch Geometry	Fassel Type

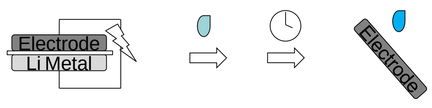
Pre-Lithiation Techniques

Direct Contact



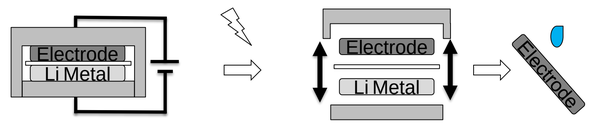
Stack of Electrode & Lithium Metal Foil — Wetted with Electrolyte, Contact for 5, 10, 20 or 30 min — Rinsed with Dimethyl Carbonate

Electrical Contact



Stack of Electrode, Separator & Lithium Metal Foil — Wetted with Electrolyte, Contact for 10, 20 or 30 min — Rinsed with Dimethyl Carbonate

Electrochemical



Li Metal Cell Setup — Discharge to 200, 150 or 100 mV — Dis-assembly — Rinsed with Dimethyl Carbonate

Results

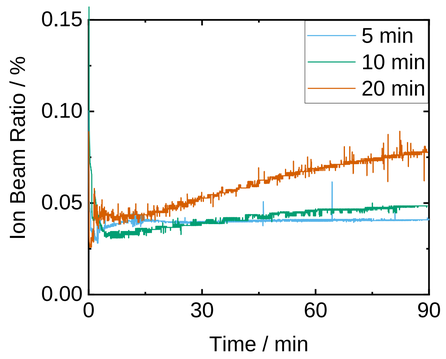
Determination of Lithium Depth Distribution *via* GD-SF-MS

- Inhomogeneous pre-lithiation
- Increasing lithium gradient with higher lithium concentration

Determination of Lithium Bulk Concentration *via* ICP-OES

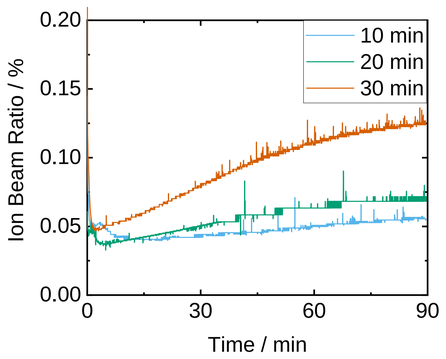
- Compensation of ALL on negative electrode needs direct contact time between 10-15 minutes, electrical contact time between 15-20 minutes and discharge cut-off voltage <100 mV

Direct Contact



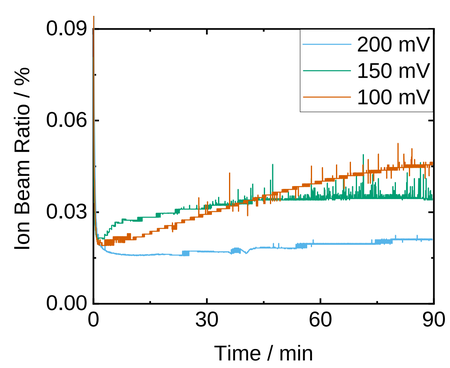
Time	Lithium Content / wt%
Aged Cell	1.23 ± 0.03
5 min	1.12 ± 0.06
10 min	1.19 ± 0.05
20 min	1.55 ± 0.08

Electrical Contact



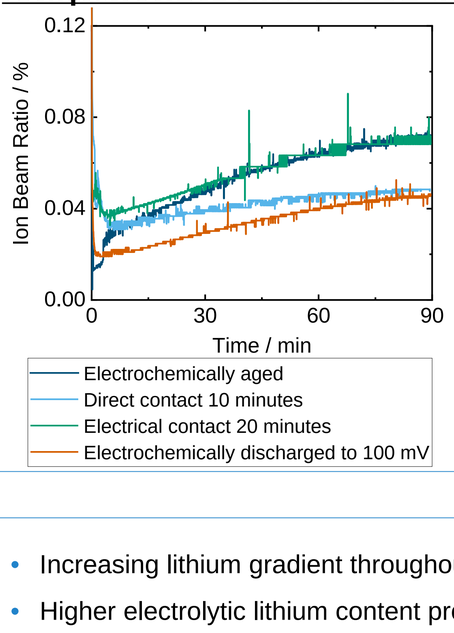
Time	Lithium Content / wt%
Aged Cell	1.23 ± 0.14
10 min	1.05 ± 0.19
20 min	1.27 ± 0.45
30 min	1.69 ± 0.31

Electrochemical



Cut-Off Voltage	Lithium Content / wt%
Aged Cell	1.23 ± 0.14
200 mV	0.52 ± 0.04
150 mV	0.60 ± 0.03
100 mV	1.11 ± 0.01

Comparison of Different Pre-Lithiation Techniques with an Electrochemically Aged Cell



Direct Contact

- ✓ Easy & fast application
- ✓ Most uniform depth profile
- × Unknown influence of pressure
- × Sticking of carbon on lithium metal foil
- × Inhomogeneous lateral distribution

Electrical Contact

- ✓ Easy & fast application
- × Low reproducibility
- × Differences in lithium depth distributions
- × Electrodes shifted while pre-lithiation

Electrochemical

- ✓ High reproducibility
- ✓ Comparably less electrolyte
- ✓ Similar electrolytic lithium content as electrochemically aged cells
- × Reassembling of the cell needed
- × Cracking of the carbonaceous electrodes

Conclusions / Outlook

- Increasing lithium gradient throughout the cell with higher lithium content
- Higher electrolytic lithium content produced more homogeneous lithium distribution
- Direct contact pre-lithiation produced the most uniform lithium distribution throughout the electrode
- Electrochemical pre-lithiation produced the most reproducible lithium content
- Identification of the most favorable direct contact time or discharge voltage, respectively, to compensate the ALL on an negative electrode
- Investigation of the influence of cycling on lithium depth distribution of pre-lithiated electrodes
- Determination of electrolytic lithium distribution throughout the cell with ^6Li enriched electrolyte

Literature

[1] Y. Liang, C.-Z. Zhao, H. Yuan, Y. Chen, W. Zhang, et al., *InfoMat* **2019**, *4*, 54.

[2] B. Vortmann-Westhoven, M. Winter, S. Nowak, *J. Power Sources* **2017**, *346*, 63.

[3] F. Holtstiege, P. Bärmann, R. Nölle, M. Winter, T. Placke, *Batteries* **2018**, *4*, 4.

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