Recent Advances in the Intercalation Battery Mechanistic Modeling Approach

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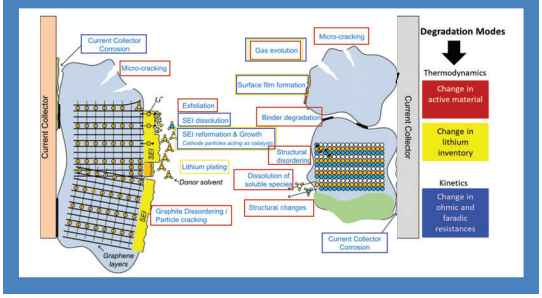
Introduction

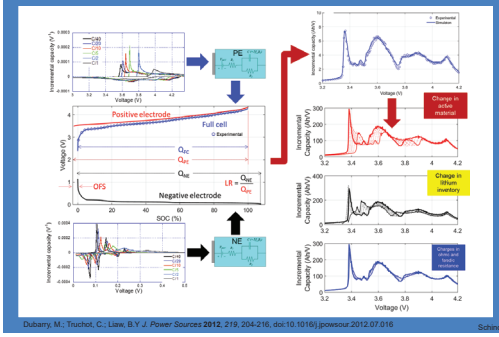
While relatively young, the mechanistic modeling approach has proven **extremely versatile and effective** for Lithium-ion battery diagnosis and prognosis.
It is a **backward-looking modeling approach** relying on **digital twins** built from **different matchings of the electrode individual voltage responses**.
The digital twins enable quantification of the **degradation modes** and open the gate for **material-based diagnosis and prognosis** without the need for complex models.
The method allowed to conceptually **explain counter intuitive concepts** such as hidden degradation mechanisms, overdischarge induced capacity, and the sudden apparition of knees.
Looking forward, the approach can still be improved and some **new directions** will be detailed here for the first time with **proof-of-concept simulations**.
This includes more varied synthetic datasets, **blended and inhomogeneous electrodes** and packs, voltage fade, as well as **calculations outside of constant current**.
These new features could allow a much wider field implementation of **better diagnosis and prognosis tools for deployed systems**.

Degradation mechanisms vs. degradation modes

Degradation modes refer to the **impact** of a mechanism **rather than its root cause**.
Every degradation mechanism will impact the amount of material able to react, the amount of lithium able to go back and forth between the electrodes, and/or the overall reaction kinetics.
As such, three main families of degradation modes can be defined: **loss of active material (LAM), loss of lithium inventory (LLI), and kinetics changes**.
LAMs and kinetic limitations must be decomposed further at the electrode or electrode component levels for blends.
Kinetic limitations must also address polarization and transport separately.



Full cell emulation is based on **half cell data** for each electrode (or each component of a blend) **at different rates.**
It only requires **few parameters**:
- The **loading ratio (LR)** that corresponds to the electrodes capacity ratio
- The **offset (OFS)** that corresponds to the electrode slippage,
- The **rate** for each electrode (or component of the blend),
- The **resistance** for each electrode (or component of the blend).



Dubarry, M.; Truchot, C.; Liaw, B.Y *J. Power Sources* **2012**, *219*, 204-216, doi:10.1016/j.jpowsour.2012.07.016

Cell degradation emulation using Digital Twins

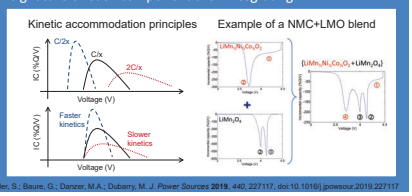
LAMs are emulated by changing the size of one electrode (or component of the blend) compared to the other(s) and by adjusting the rate to account for changes in current density.

LLI is emulated by increasing the offset. This is because LLI is increasing the slippage between the electrodes.

Ohmic resistance changes are emulated by translating the voltage responses up or down.

Faradic resistance changes are emulated by adjusting the rate and the resistance together. To simulate faster/slower kinetics data at a slower/faster rate is used then polarization is adjusted so that the overall resistance stayed the same.

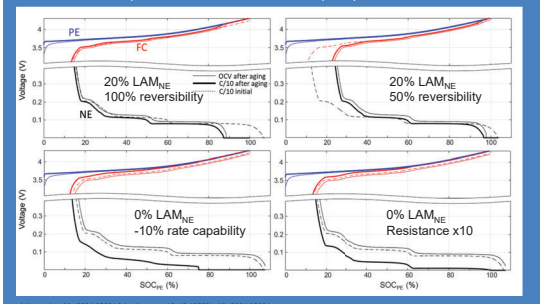
Blends are currently emulated by summing the pondered IC signature of each component then integrating.



Schindler, S.; Baure, G.; Danzer, M.A.; Dubarry, M. *J. Power Sources* **2019**, *440*, 227117, doi:10.1016/j.jpowsour.2019.227117

Li plating & hidden mechanisms

With a mechanistic view, plating can only originate from **two pathways**:
NE full before PE is empty or **NE potential < Li^0/Li^+ potential**
Plating does not induce capacity loss but turns the **NE into a blended electrode**.
Irreversible plating = LLI and different reversibilities can be simulated.
The mechanistic approach was proven efficient to simulate and forecast plating as well as some of the possible accelerations in the capacity loss .



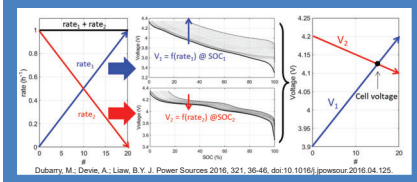
Attia *et al.*, arXiv:2201.02891 [physics.app-ph] ,10.48550/arXiv.2201.02891
Anseán, D. *et al.*, J. Power Sources 2017, 356, 36-46, doi:10.1016/j.jpowsour.2017.04.072
Baure, G.; Dubarry, Batteries 2019, 5, doi:10.3390/batteries5020042

Blends & Voltage fade

Many commercial cells started to use **blended electrodes**, whether on the positive or negative electrodes.
The approach in the present model implies that the **current has to be constant on both component of the blend** throughout the entire SOC range
Recent work by Heubner *et al.* showed that the **reality is more complex** and that three case figures needs to be considered:
- **separated voltage responses** (e.g. LFP+LMO)
- **mostly overlapping responses** (e.g. NMC +NCA)
- **partially overlapping responses** (e.g. NMC+LMO or Gr+SiOx)

Present approach is **not accurate for 2nd and 3rd cases**

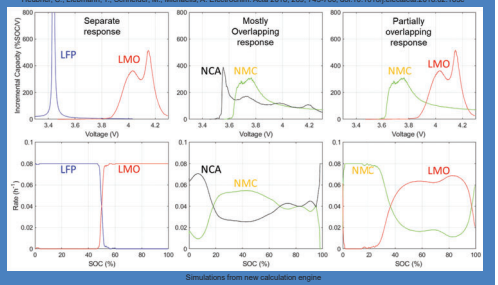
The mechanistic approach can be upgraded with the implementation of a **paralleling model** to be more accurate.

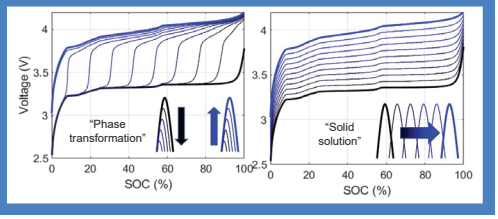


Dubarry, M.; Devie, A.; Liaw, B.Y. J. Power Sources 2016, 321, 36-46; doi:10.1016/j.jpowsour.2016.04.125.

Blend simulations also allow to remove one of the approach requirements: the invariancy of the voltage response with time.
If variable, **phase transitions or solid solutions** evolutions could be taken into consideration as **blends with varying ratio**.

Heubner, C.; Liebmann, T.; Schneider, M.; Michaelis, A. Electrochim. Acta 2018, 269, 745-760, doi:10.1016/j.electacta.2018.02.165c

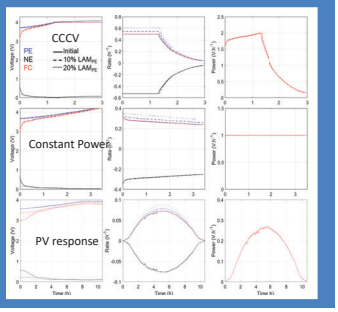




Non-constant current

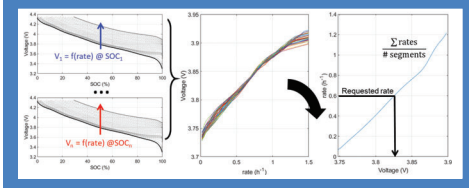
While most usage of the mechanistic approach is done for constant current, this is not a prerequisite. Other duty cycles could allow to investigate impact of degradation modes on **constant power or constant voltage steps**. It could allow to apply the approach on deployed systems with semi constant cycles or to optimize charges based on electrodes cutoffs.

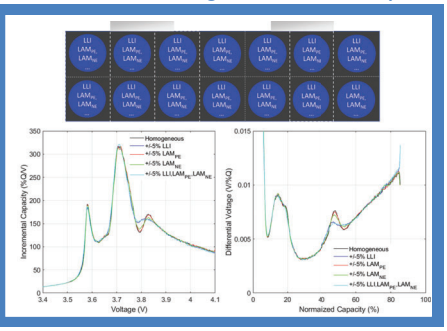
Using the ability to simulate different rates, the mechanistic approach can be adapted to **simulate different duty cycles.** By aggregating charge and discharge curves at different rates, data following a specific non current constant evolution can be selected for each SOC and the full V vs. SOC response can be constructed point by point.



Inhomogeneous electrodes / packs

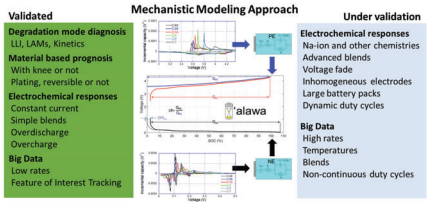
With the manufacturing of larger and larger single cells and packs, the electrochemical behavior of electrodes, or single cells, was shown to be inhomogeneous. **Paralleling several mechanistic models** could allow to investigate the impact of cell-to-cell variations, inhomogeneities in degradation, localized defects, or lithium reservoirs on the response of the full electrode using a **segmented cell digital twin** where each segment is individually parameterizable.





Conclusions & Perspective

- ✓ Mechanistic approach is an extremely versatile and effective for Lithium-ion battery diagnosis and prognosis.
- ✓ Enables quantification of degradation modes with material-based prognosis without the need for complex models, protocols, nor instrumentation.
- ✓ Allows to explain counter intuitive concepts such as hidden degradation mechanisms, overdischarge induced capacity, and sudden apparition of knees.
- ✓ New features could be implemented to widen the applicability of the approach (advanced blends, inhomogeneities, dynamic simulations,...)



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