Delivering *operando* insights into the causes behind capacity degradation in aged Ni-rich layered cathodes using charge photometry[1]

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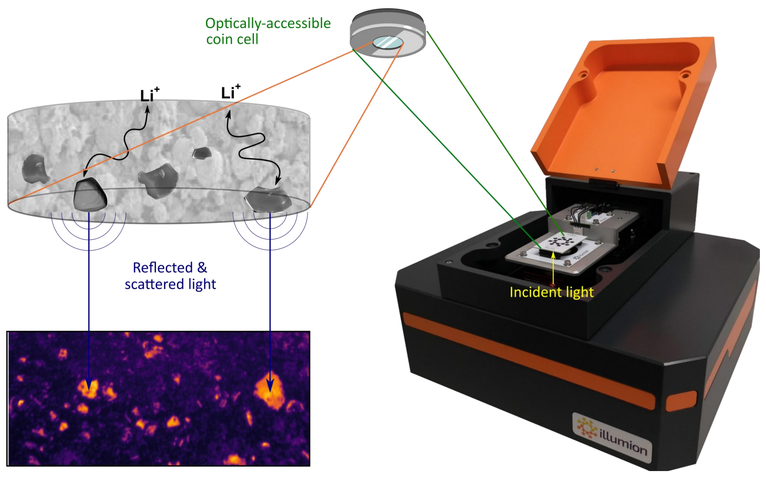
Capacity degradation in Ni-rich NMC cathodes

- Ni-rich $LiNi_xMn_yCo_{(1-x-y)}O_2$ (NMC) cathodes are hindered by cycling stability issues, but traditional techniques for studying the degradation mechanisms responsible are only sensitive to the ensemble system and/or do not provide much information on the dynamic processes involved
- Here, we introduce **charge photometry**: an innovative imaging technique which delivers crucial insights into the changes to ion transport behaviour within **individual** active particles **during cycling**



Charge photometry images the electrode during battery operation, tracking local changes to **state-of-charge** & **morphology** with **single particle resolution**

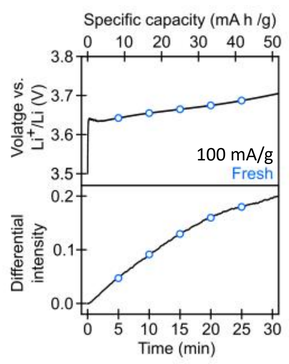
- Scattering intensity of active particles tracks the changing state-of-charge as the electrode is charged & discharged in the instrument
- The amount of light scattered depends on the active material's electronic structure, which is altered upon ion (de)intercalation[2]
- Material agnostic

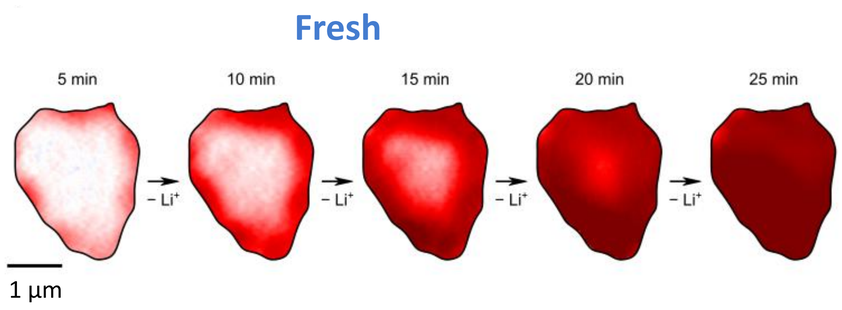
Capturing Li-ion dynamics on the single particle level

At near-full Li-content, the Li-ion diffusivity in NMC is initially low and increases upon delithiation.[3] This results in pronounced Li-ion gradients within active particles at the beginning of delithiation, which can be observed using charge photometry.[4]

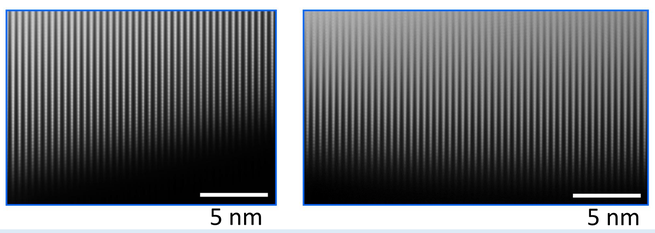
Fresh electrode, single-crystal NMC ($LiNi_{0.88}Mn_{0.05}Co_{0.07}O_2$)

At the beginning of delithiation, Li-poor regions grow symmetrically from the edges of the particle in a 'shrinking core'-like behaviour





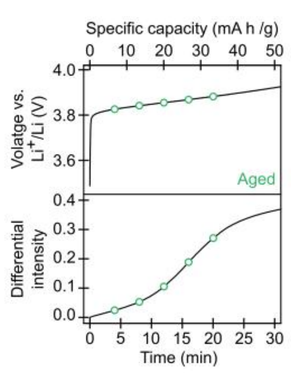
Open layered channels observed in the fresh NMC particles

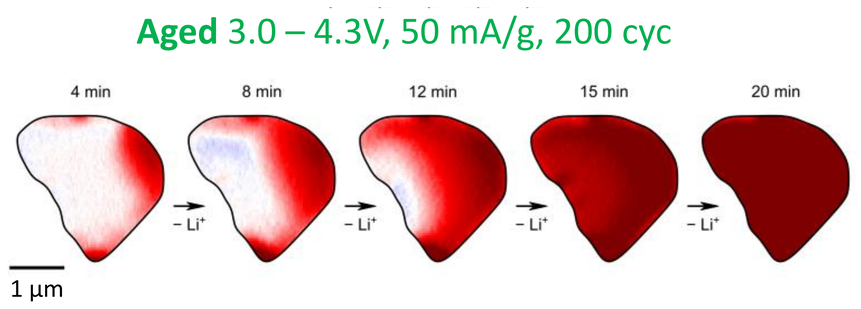


HAADF-STEM imaging

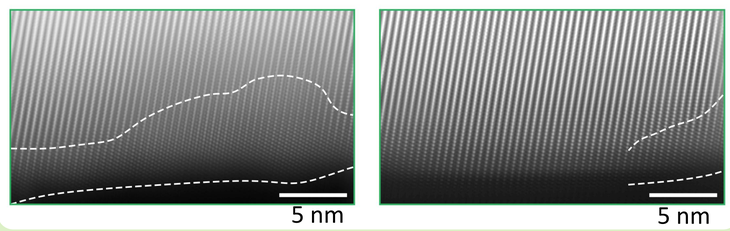
Aged electrode, single-crystal NMC ($LiNi_{0.88}Mn_{0.05}Co_{0.07}O_2$)

At the beginning of delithiation, Li-poor regions initially form unevenly around the particle edge & the remaining Li-rich region is displaced from the centre





Rocksalt forms on the edges of the aged particles, with a large variation in layer thickness within a single particle

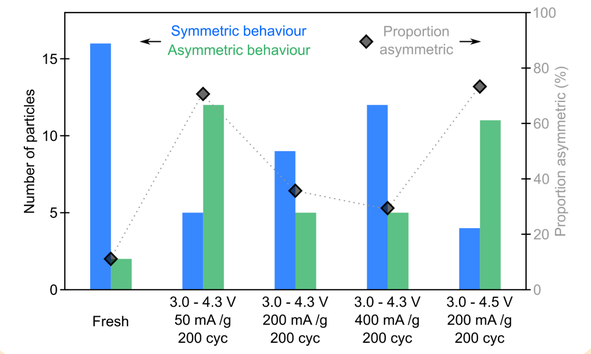


HAADF-STEM imaging

Asymmetric delithiation in aged NMC particles is attributed to the uneven rocksalt layer, which impedes the transport of Li-ions over parts of the active surfaces

Comparing aging conditions

Aging cycles with deeper delilthiation (either via a slow cycling rate or a higher cutoff voltage) have the highest proportion of particles with asymmetric delithiation behaviour and the worst rate capabilities



Outlook

- Asymmetric delithiation due to uneven rock-salt formation contributes to degradation of rate capability & capacity in aged Ni-rich NMC cathode materials
- Modifications (*e.g.* uniform coatings) to promote uniform delithiation and tackle rocksalt formation are important for improving the long-term stability & rate capabilities of Ni-rich cathodes
- Tracking Li-ion dynamics on the single particle level using charge photometry unlocks the possibility of truly understanding the impact of such modifications in the quest for electrode optimisation

References:

[1] *Z. Lun et al.*, ***Energy Environ. Sci.***, 18, 4097-4107 (2025)

[2] A.J. Merryweather *et al.*, ***Nature***, 594, 522-528 (2021)

[3] K. Märker *et al.*, ***Chem. Mater.***, 31, 7, 2545–2554 (2019)

[4] C. Xu *et al.*, ***Joule***, 6, 2535-2546 (2022)

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