Investigating changes in kinetics and transport over NCA/Gr-SiO$_x$ battery lifetime

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1. Background

- A number of model parameters are affected by battery ageing, but conventional parameterisation of the anode and cathode is no longer possible.

Hypothesis: It is possible to maintain model accuracy throughout battery lifetime via parameter optimisation, without inclusion of degradation models

- Objective 1: Identify the main degradation modes appearing in three groups of cells via DVA and track kinetic and transport changes throughout battery lifetime via model parameter adjustment.
- Objective 2: Compare identifiability of selected parameters when diffusion is a function of stoichiometry versus a constant.

Knowledge gap

- All electrochemical models are sensitive to the value of the diffusion ($D_\pm$), which varies with concentration, but in most cases it is taken as a constant or adjusted between datasets to match experimental results.
- $D_\pm$ measurement methods are questionable.
- With the (ir)reversible morphological changes experienced by the particles (e.g. cracking or volume expansion) the Fickian diffusion is expected to change as well.

2. Methods

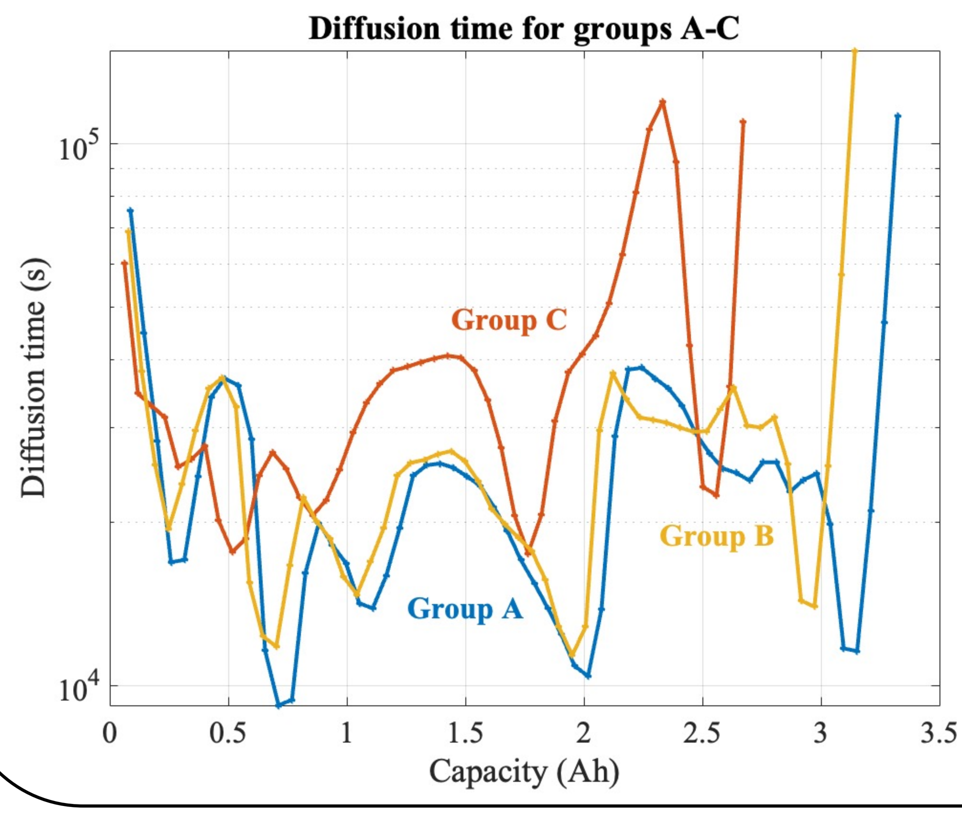
Pristine	Calendar ageing → LLI 12 months at 45 °C	Cyclic ageing → LAM$_{NE}$, LAM$_{PE}$, LLI 12 months at 45 °C
Group A 100 % SOH	Group B 93 % SOH	Group C 80 % SOH

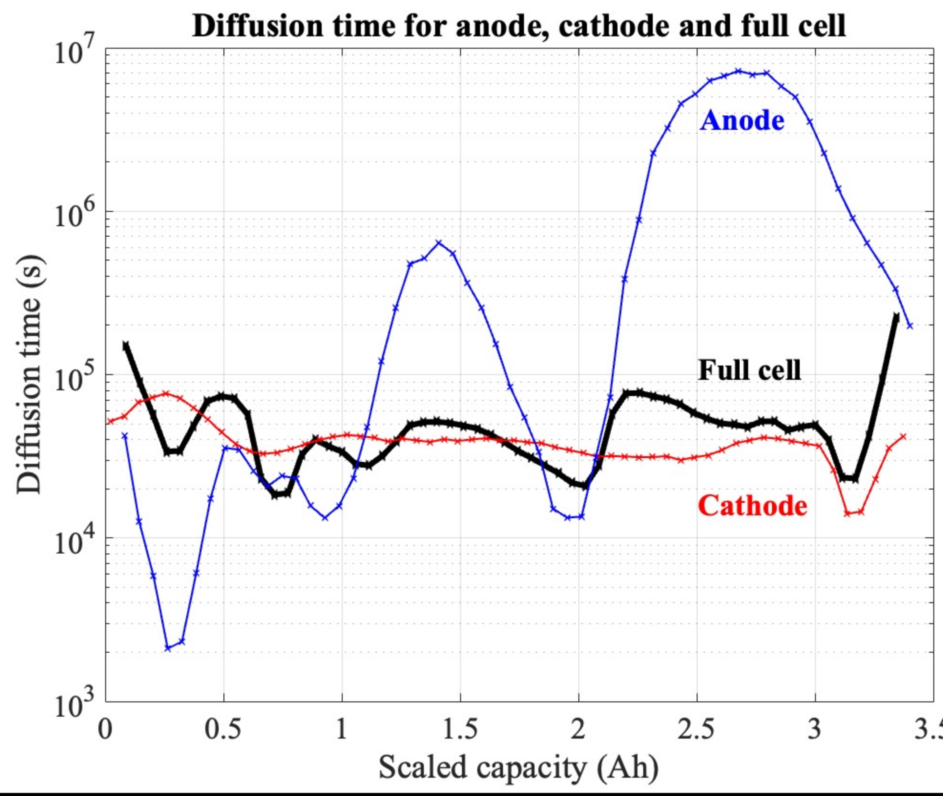
* 3 months relaxation at 23 °C in between (due to COVID-19)

- Parameters affected by ageing:
  - stoichiometric limit x_-
  - diffusion time t_{D_-}
  - kinetic rate constant k_-
  - active material volume fraction $\varepsilon_{s\,-}$
- Diffusion time increases as battery ages.

$$t_{D_\pm} = \left(\frac{\lambda_{D\pm} D_\pm}{R_\pm^2}\right)^{-1} = \frac{4}{\pi}\left(\frac{I}{3FAL_\pm}\frac{\mathrm{d}U_\pm/\mathrm{d}c_\pm}{\mathrm{d}V_\pm/\mathrm{d}\sqrt{t}}\right)^{-2}$$

- Diffusion ageing parameter λ_{D_-} is introduced to account for any diffusive or morphological changes induced by ageing.





3. Results: parameter optimisation for an isothermal SPM for aged cells

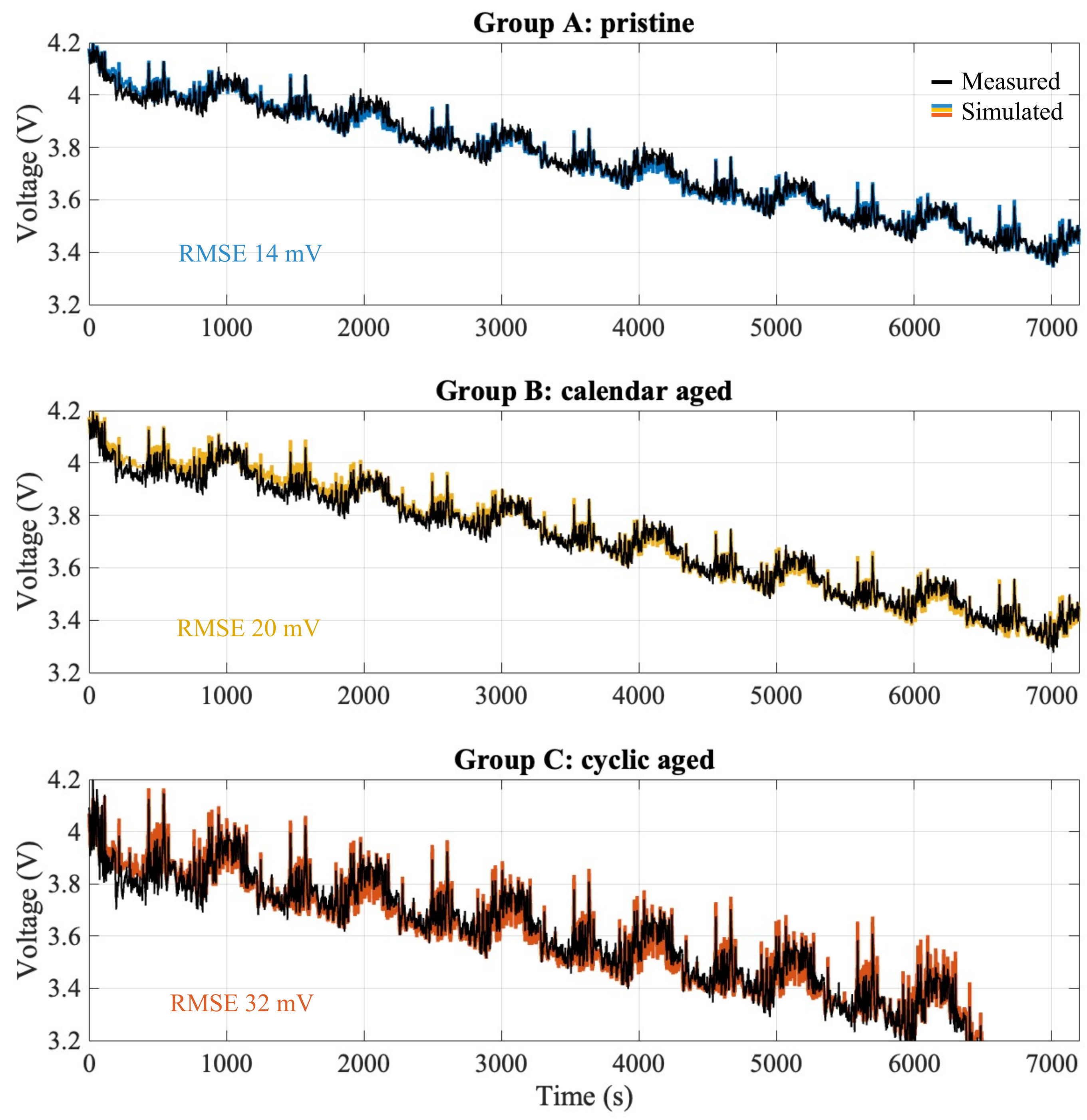
- An isothermal single particle model (SPM) is simulated in COMSOL Multiphysics® with MATLAB® via LiveLink™ using the Artemis motorway drive cycle.

$$C_{\mathrm{Df}} = \begin{array}{c} \begin{matrix} x_- & \varepsilon_{S-} & k_- & \lambda_{D_-} \end{matrix} \\ \begin{bmatrix} 1 & . & . & . \\ 0.43 & 1 & . & . \\ 0.47 & 0.54 & 1 & . \\ 0.40 & 0.52 & 0.54 & 1 \end{bmatrix} \end{array} \qquad C_{\mathrm{Dc}} = \begin{array}{c} \begin{matrix} x_- & \varepsilon_{S-} & k_- & \lambda_{D_-} \end{matrix} \\ \begin{bmatrix} 1 & . & . & . \\ 0.80 & 1 & . & . \\ 0.83 & 0.79 & 1 & . \\ 0.83 & 0.78 & 0.80 & 1 \end{bmatrix} \end{array}$$

- Parameter sensitivity matrices C_{Df} and C_{Dc} reveal that diffusion as a function of stoichiometry (C_{Df}) improves parameters identifiability [1] , as the linear correlation between sensitivities is half the magnitude of C_{Dc} when diffusion is a function.

$$\min_p \sum_{i=1}^{N_t} \left(E_i^{\mathrm{sim}} - E_i^{\mathrm{exp}}\right)^2$$
$$p = \{p_1, p_2, \dots p_n\},$$
$$p_k^l \leqslant p_k \leqslant p_k^u$$

Optimisation parameter	Group A	Group B	Group C
x_-	0.74	0.65	0.65
ε_{S-}	0.875	-	0.83
k_-	5.5e-11	4.6e-11	1.6e-11
λ_{D_-}	1	-	0.7



- Simulation accuracy decreases with battery life, but remains acceptable (RMSE 14 - 32 mV).
- Some inaccuracy is due to cathode degradation, which is not accounted for.
- Without parameter optimisation at the end of life, the RMSE would increase to 180 mV.

4. Conclusions

- The SPM voltage prediction accuracy can be maintained throughout battery lifetime within 14 – 32 mV RMSE if the parameters are updated accordingly.
- Calendar aged: decrease in x_- to account for LLI, kinetics slows down.
- Cyclic aged: decrease in ε_{S-} related to LAM, decrease in x_- due to LLI. Both diffusion time and kinetics decrease.
- Further study: improvement of the optimisation routine, and and inclusion of silicon particle volume expansion effects.

References

[1] Moura, S.J., Chaturvedi, N.A. and Krstić, M., 2014. Adaptive partial differential equation observer for battery state-of-charge/state-of-health estimation via an electrochemical model. *Journal of Dynamic Systems, Measurement, and Control*, *136*(1).

Acknowledgements

This work was financially supported by EPSRC, Innovate UK (104183, "UK Niche Vehicle Battery Cell Supply Chain"; 104815, "Pozibot"), and the Faraday Institution (faraday.ac.uk; EP/S003053/1, grant number FIRG025).