Faraday Discussions

Supplemental information

Supporting information to:

Understanding the stability of the solid electrolyte interphase formed by vinylene carbonate and fluoroethylene carbonate in sodium-ion batteries

Jan Felix Schuster*[1], Qihan Hu[1], Laura King[1], Alexandre Linas Lapidus[1], Charles Aram Hall[1], Leif Nyholm[1], Reza Younesi*[1]

Methods – GC-MS and XPS measurements

Four additional samples were prepared to understand the interaction of VC with sodium metal. Cells with or without 2wt%VC with PW or Na-metal counter electrodes were assembled. These cells were cycled for one CV cycle according to the same limits as detailed in the main article – the cycling of the PW cells was stopped as soon as they reached 0 µA current. The CV can be seen in Figure S2 (a). The expected reduction peaks for VC were seen in the PW cell, but not the Na-metal-containing cell. The cells were stopped and immediately taken to a glove box (H_2O and O_2 <1 ppm) and disassembled. The two separators, working and counter electrode, were immersed in 1 ml of dimethyl carbonate (DMC, <99% Sigma Aldrich) for 60 minutes.

The glass vials containing DMC and cell parts were shaken occasionally to ensure a complete immersion. 500 ul of this solution was taken and dissolved in 4500 µl dichloromethane (GC grade Sigma Aldrich). These samples were centrifuged for 20 minutes at 5850 rpm to precipitate any solid components and to avoid syringe filters. 900 ul of the centrifuged sample was added with 100 ul of a 20000 µl l^{-1} (results in a 2000 µl l^{-1} concentration in the sample) tetramethyl urea (<99% VWR) stock solution, as the internal standard for the GC-MS standard.

Gas chromatography experiments were performed on a Shimadzu QP 2020 NX GC-MS which was equipped with an autosampler and mass spectrometry detector (Dual Stage TMP (QP2020)). GC-MS post-run analysis (GCMS solution version 4.53SP1) and Python were used for the data analysis. The following parameters for the analysis were used: Gas: He (Air liquid), Column: deactivated carbon guard column 1.5 m connected to SH-200MS 30 meter(inner diameter 0.25 mm and film thickness of 0.25 µm). Parameters during the injection: split ratio of 20, injection temperature of 150°C and a constant linear velocity of 35.2 cm s^{-1}. The oven was held at 40°C for 3 minutes, then the temperature was increased at 10 °C min^{-1} to 220 °C with a hold for 2 minutes. The MS inlet was held at 220 °C and the interface at 200°C and was used in the scan mode for fragments from 35 m/z to 500 m/z.

For the XPS measurements, electrodes were left in the glovebox to dry after submersion in DMC. They were subsequently cut and mounted onto an air-sensitive sample holder using conductive carbon tape and transferred to the Kratos Axis Supra+ Spectrometer under an Argon atmosphere. Spectra were measured using an Al K-α light source (1486.7 eV) and were calibrated using the C-C sp3 peak at 285.0 eV.

Model cells were assembled with a reference and working electrode (WE) on the same side of the separator (Figure S1). Placing the reference electrode and WE on the same side was done to simulate voltages with extra resistance from the separator. The two separators were taken, as well as the working and counter electrode for GC-MS, and XPS analysis.

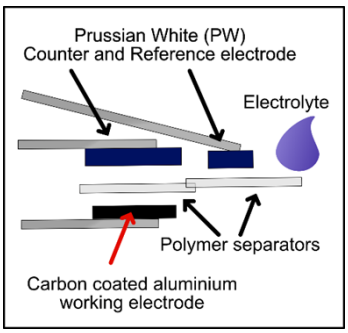


Figure S1: Schematic side view of the electrode configuration of the three-electrode pouch cells used in the measurements. The two separators were overlapping slightly to ensure contact of the reference electrode pieces to the working and counter electrode via the electrolyte.

Results and discussion

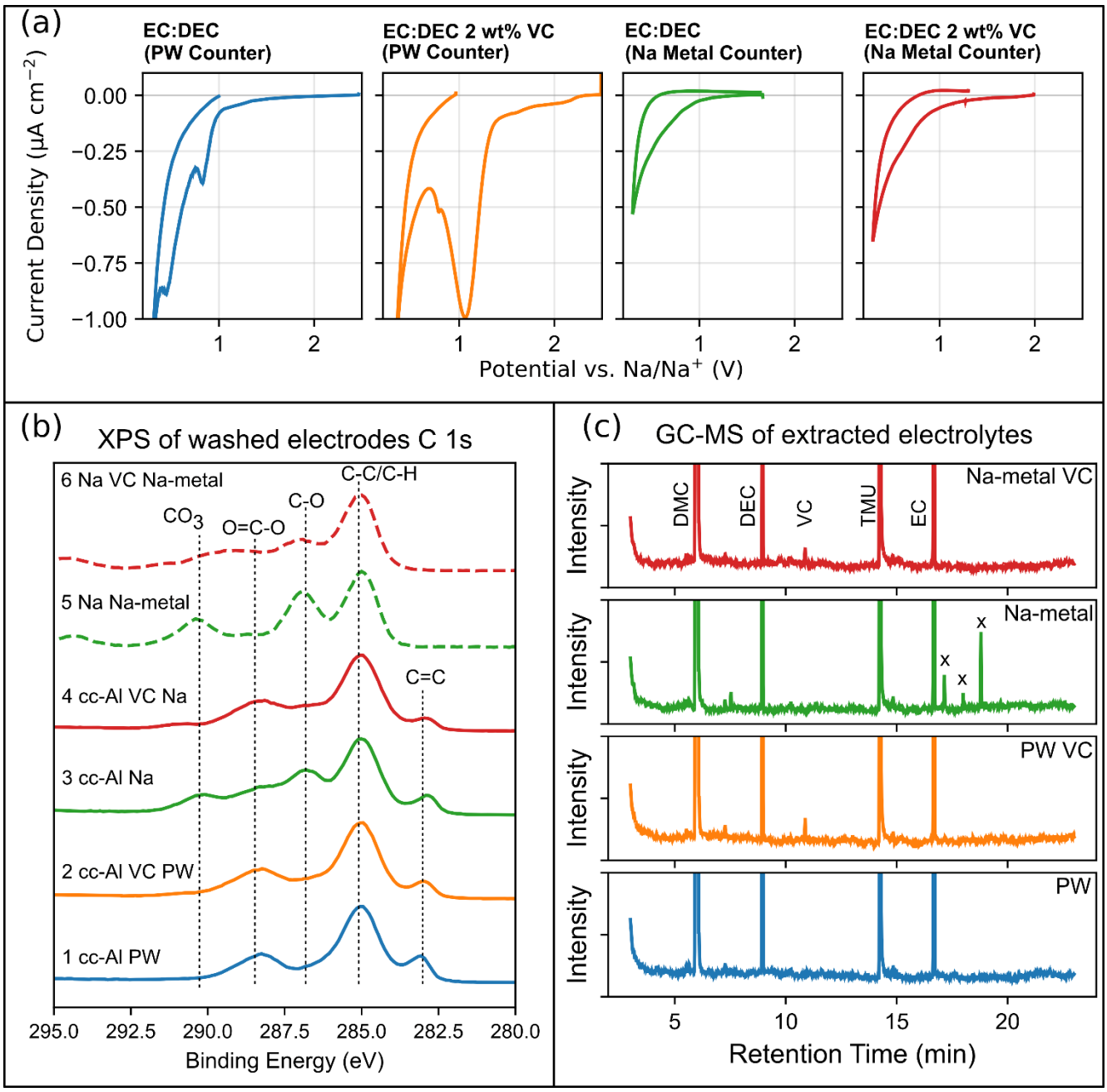
The GC-MS results of the four cells that were investigated show that the extracted electrolyte contained all the expected components, eluting in the following order: DMC 6.03 min, DEC 8.9 min, VC 10.8 min (if added), TMU 14.2 min and EC 16.7 min. The VC concentration in both VC-containing cells (with PW and Na-metal counter electrode) was similar based on the area ratio to the internal standard TMU. In the case of 1 M $NaPF_6$ EC:DEC with Na-metal, there were additional peaks (marked with an X in Figure S5 (c) eluting at 17.1 min, 17.9 min and 18.8 min. The retention times and the mass fragments do not allow direct identification; however, they indicate that these are degradation products formed from the solvents. Possible degradation products include Diethyl-2,5-dioxahexane dicarboxylate, which was identified in other studies as a typical degradation product[1]. The mass fragments indicate a high similarity to the carbonate solvents.

The C 1s spectra recorded with XPS for the carbon-coated aluminium working electrodes, as well as the sodium metal counter electrodes, all show peaks indicating C-C/C-H bonds, which usually are attributed to solvent residues, SEI species and the carbon present in parts of the electrode. Additionally, the carbon-coated electrodes show a peak due to the carbon double bond. Additional SEI species bonds C-O, O=C-O, and CO_3 were assigned based on previous work on the $NaPF_6$ EC:DEC system by Fondard et al[2]. The XPS results also indicate the presence of VC oligomers and polymers at around 291.3 eV, based on results reported for the lithium equivalent of this reaction.[3]

Comment [LN]: Which components were expected?

Comment [LN]: Which cells?

Comment [LN]: Unit missing! eV!



S2: (a) Cycling voltammograms of model cells with carbon-coated aluminium working electrodes and Prussian white or sodium metal counter electrodes with 1 M $NaPF_6$ EC:DEC, with and without 2 wt.% VC. Four cells were investigated: baseline EC DEC with PW (blue), PW with 2 wt% VC (orange), EC DEC with Na-metal (red) and Na-metal with VC (red). (b) Samples 1 to 4 show the spectra for carbon-coated working electrodes after DMC washing (colour code is the same as in (a), while 5-6 (dotted lines) show the spectra of the sodium metal surface after washing with and without VC present. (c) Enlarged y-axis gas chromatograms showing the total ion count as intensity of the cells shown in (a). The cell containing no VC and sodium metal showed additional peaks (marked with x); the other cells showed peaks showing all the electrolyte components, as well as minor impurities.

When increasing the VC concentration to 10 wt.%, the VC reduction peak is observed (Figure S4). VC reacts spontaneously with the Na-metal also in this case. The reduction products are adsorbed on the Na-metal surface. The local concentration of VC on the working electrode is lowered, and the VC reduction peak is not observed (see Figure S4 Na metal with 2 wt.% VC). The XPS results show that there was a thin VC film, even though the CV results do not clearly indicate this. The poly-VC peak around 291 eV is very minor but visible. When the electrolyte was extracted by washing the electrodes and separator with DMC, VC was still detected (Figure S5 (c)). This indicates that VC was present even in the sodium metal-containing cell but not necessarily available for reduction. When a larger amount of VC was added, there was a VC reduction peak on the first cycle, but this peak then disappeared. A VC containing SEI layer was being formed based on the XPS of the cc-Al in the cells (Figure S2 (b) sample 4),

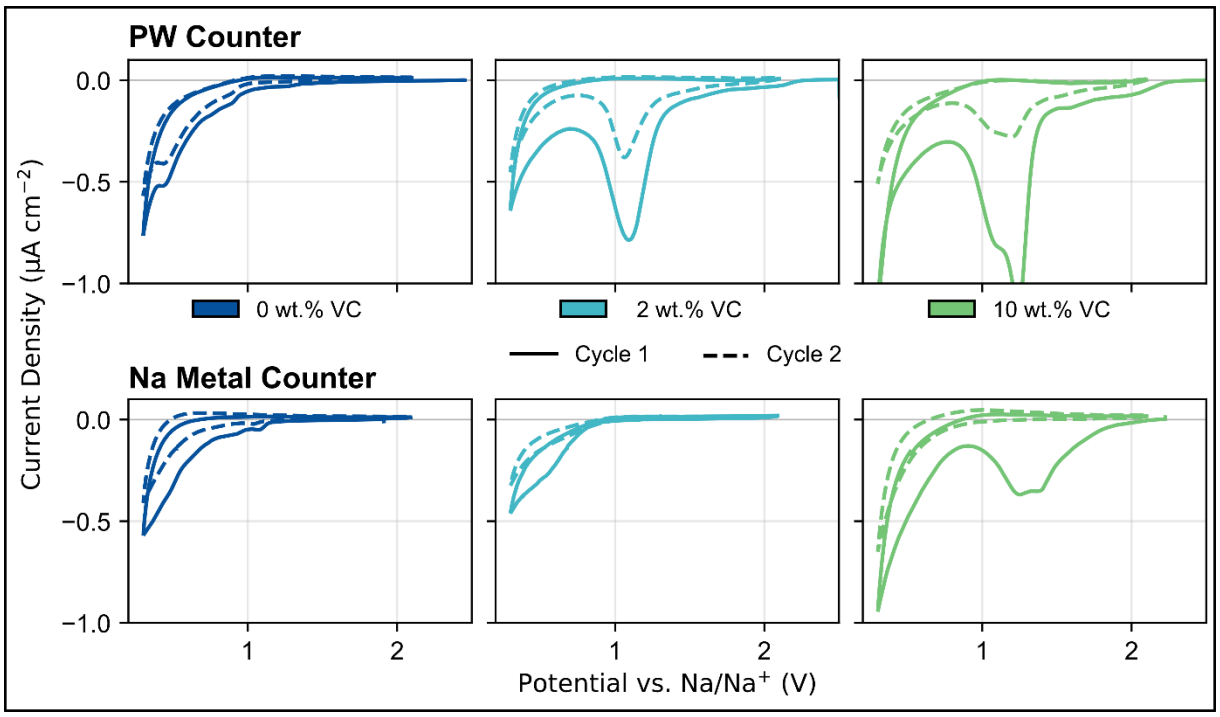


Figure S3: Cyclic voltammograms of model cells with varying concentrations of VC (0, 2 and 10 wt.%) in a 1 M $NaPF_6$ EC:DEC electrolyte with Prussian white (top row) and sodium-metal (bottom row) counter electrodes. Cycles 1 and 2 are shown using full and dotted lines, respectively. A clear VC decomposition peak was apparent after adding 10 wt.% VC to the 1 M $NaPF_6$ EC:DEC electrolyte in both systems.

Studies of the SEI formation are highly sensitive to the substrate used, as seen in Figure S2. There was a large difference between the reduction and oxidation capacities when the capacity shifted from aluminium to copper current collectors. The main difference is the additional reactions introduced by the copper current collector; copper oxide will be reduced in the presence of sodium. The thickness of the carbon coating was 1 µm in both cases, and the large difference in the CVs can be explained by copper having an electroactive copper oxide layer. It is therefore difficult to use copper substrates in this type of model cell.

(1) $Cu_2O + 2e^- + 2Na^+ \leftrightarrows 2Cu + Na_2O$ (2) $CuO + 2e^- + 2Na^+ \leftrightarrows Cu + Na_2O$

These reactions can be seen in the CVs of the copper substrates which are partially reversible and overlap with SEI formation, this makes is hard to analyze the SEI formation (Figure S2).

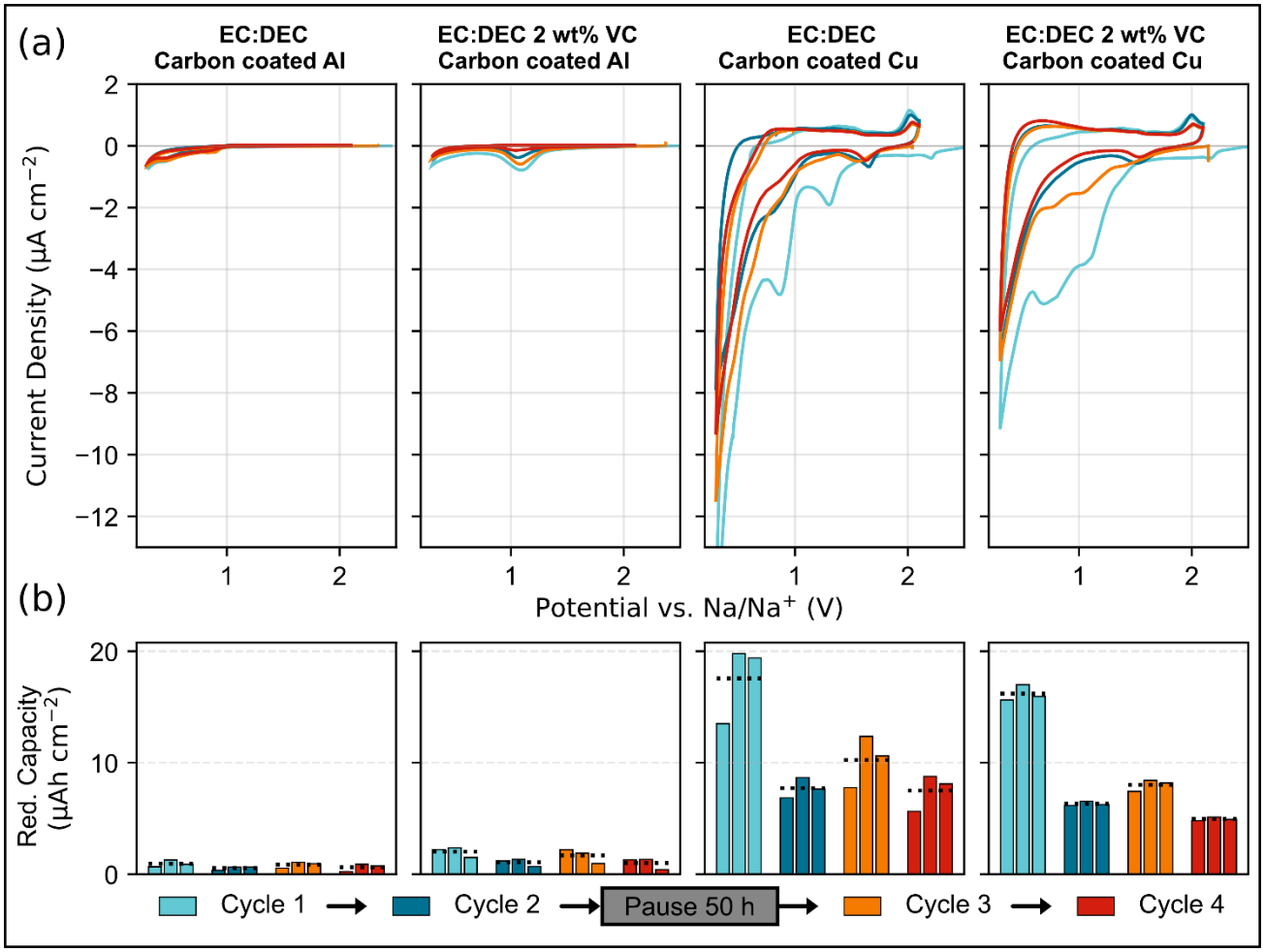


Figure S4: Comparison of CV scans in cells containing carbon-coated aluminium and carbon-coated copper foil working electrode for 1 M $NaPF_6$ EC:DEC with and without 2 wt.% VC additives. Cells shown for carbon-coated aluminium are shown as well in figures 2 and 3 – data is shown for ease of comparison.

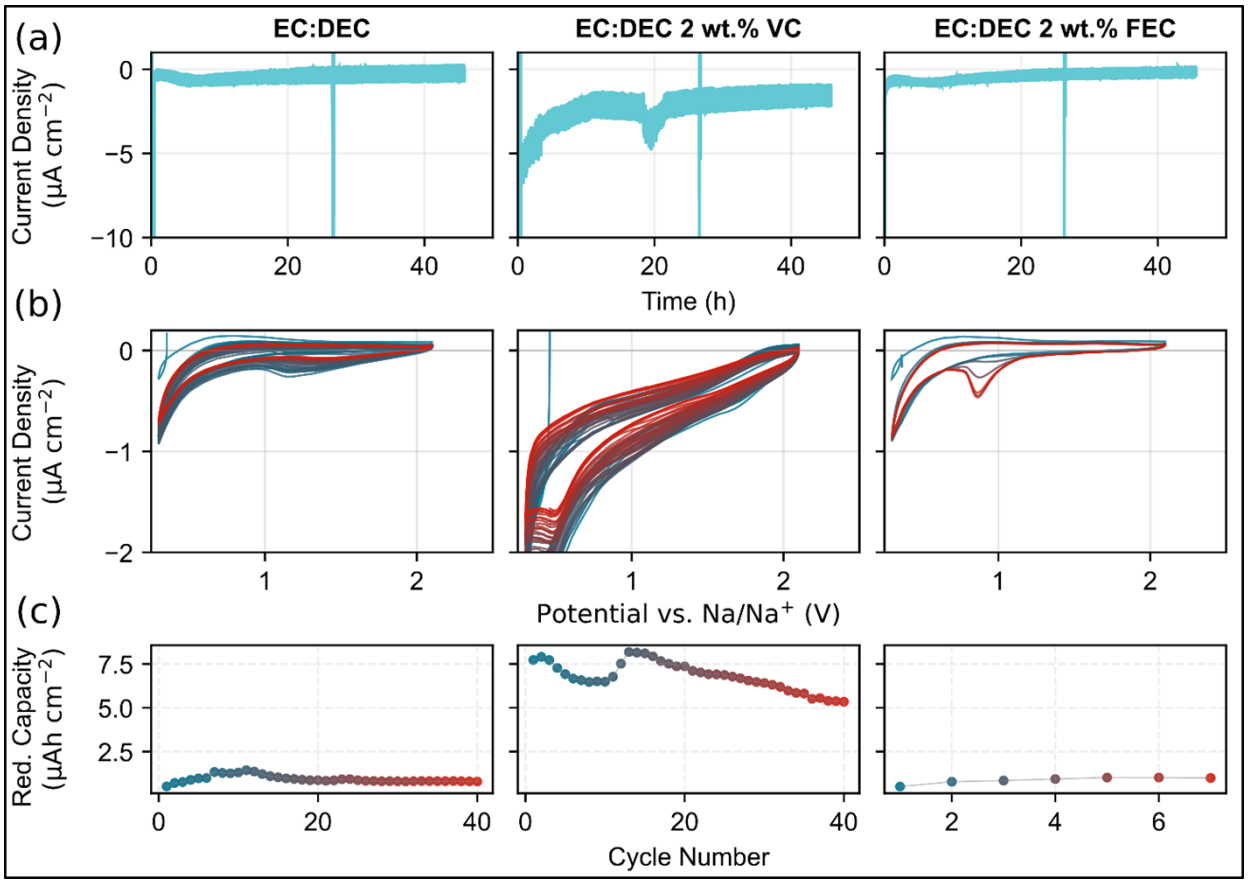


Figure S5: Replicas of the cells presented in Figure 6, a) Areal current density for a potential step experiment at 300 mV with a duration of more than 40 hours for a carbon-coated working electrode in 1 M $NaPF_6$ EC:DEC (1:1 v:v) with and without 2 wt.% of either VC or FEC. b)Subsequent testing of the SEI stability by continuous CV cycling. c) Areal reduction capacity versus cycle number (cycle numbers shown as a gradient from dark blue (cycle 1) to red (cycle 40)).

References

1 A. Hofmann, F. Müller, S. Schöner and F. Jeschull, *Batteries & Supercaps*, 2023, **6**, e202300325.
2 J. Fondard, E. Irisarri, C. Courrèges, M. R. Palacin, A. Ponrouch and R. Dedryvère, *J. Electrochem. Soc.*, 2020, **167**, 070526.
3 L. E. Ouatani, R. Dedryvère, C. Siret, P. Biensan, S. Reynaud, P. Iratçabal and D. Gonbeau, *J. Electrochem. Soc.*, 2008, **156**, A103.
1