

## Electronic supplementary information

### Comparative stability of the solid electrolyte interphase in potassium and sodium batteries

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#### Experimental section

**Cell assembly:** All the cell assemblies were carried out in an argon-filled glovebox ( $O_2 < 1$  ppm,  $H_2O < 1$  ppm). Platinum (Pt) discs (10 mm diameter, 0.1 mm thickness, Goodfellow) were cycled against Na- or K-metal discs pressed on aluminium foil (13 mm diameter) in pouch cells. The cells used 150  $\mu$ l of 1 M  $NaPF_6$  (Stella) or 1 M  $KPF_6$  (Sigma) dissolved in a 1:1 volume mixture of ethylene carbonate (EC, BASF) and diethylene carbonate (DEC, BASF). Na- or K-conductive  $\beta$ -alumina (Ionotech, 20 mm diameter, 1 mm thickness) or Solupor® (Lydall – 3PO7A) separators were used. An illustration of the cell setup is shown in Fig.1.

**Electrochemical testing:** Galvanostatic experiments were done using a Novonix high-precision cycler system at 30 °C. The cells were cycled from 0.1 V to 1.5 V vs.  $Na^+/Na$  or  $K^+/K$  with a constant current of 3  $\mu$ A (3.8  $\mu$ A per  $cm^2$ ). It is expected that the theoretical surface area (flat surface) of the platinum disc and the practical surface area are almost equal. The surface area of typical carbonaceous materials has previously been reported as  $2-10\ m^2\ g^{-1}$ .<sup>2</sup> Using  $2\ m^2\ g^{-1}$  for a mass loading of 10 mg per  $cm^2$  this correlates to around C/4 for a battery cell. Therefore, the current is ideal to test “realistic” rates for forming SEI. The cut-off potential was set to 0.1 V to avoid underpotential deposition of sodium and potassium. After 5 cycles, the cells were rested at open circuit potential for 50 hours with no external current or potential applied.

**X-ray photoelectron spectroscopy (XPS):** The measurements were done using Kratos AXIS Supra+. The SEI on the negative electrode was probed after 5 cycles, before and after a 50-hour pause. Two cells were cycled five times for each electrolyte system, whereas one was stopped after five cycles at 0.1 V (before the pause sample) and one after a pause of 50 h (after the pause sample). The cells were disassembled in an argon-filled glovebox, the electrodes were rinsed with dimethyl carbonate (DMC), and then transferred to the XPS via a vacuum container. The samples were measured using two different photon energies of 1487 eV and 2984 eV from Al K $\alpha$  and Ag L $\alpha$  sources, respectively. All spectra are normalized to the sp<sub>3</sub> C-C carbon at 284.9 eV.

**Nuclear magnetic resonance spectroscopy (NMR):** All samples were prepared in an argon-filled glovebox. For each system (Na and K) four different samples were prepared. First, the pristine electrolyte was mixed with 750  $\mu$ l deuterated dimethyl sulfoxide (DMSO-d6). The three other electrolyte samples were extracted from the Solupor separator from an assembled cell, cell after 5 cycles and cell after 50 h pause. The separator was dipped in 750  $\mu$ L DMSO-d6 and then manually shaken. The DMSO-d6 should act as a potent solvent to extract most the decomposition products from the separator and electrolyte. 700  $\mu$ L of the solution was filled into

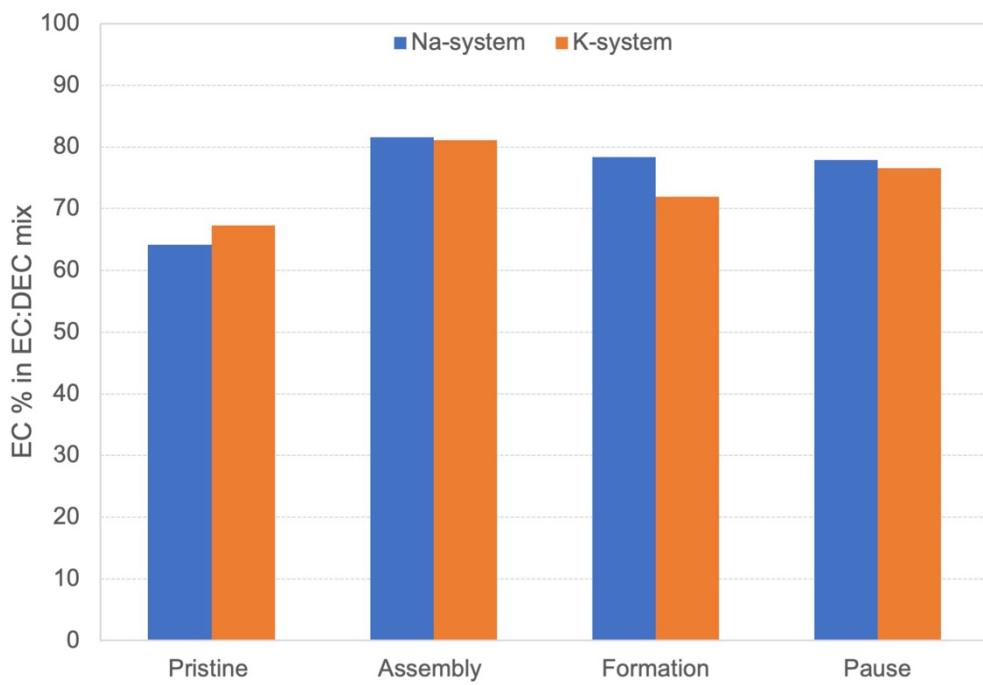
NMR tubes fitted with J-Young taps. Experiments were carried out on a Bruker Avance IIIHD spectrometer equipped with either a 9.4 T ( $\nu_0(1H)$  = 400 MHz) or 11.7 T ( $\nu_0(1H)$  = 500 MHz) magnet. A Bruker BB Smartprobe (400 MHz) or BBFO Smartprobe (500 MHz) was used.

**Table S1**  $^1\text{H}$ -NMR solvent peaks and their integration values normalized for each EC peak in the Na-system.

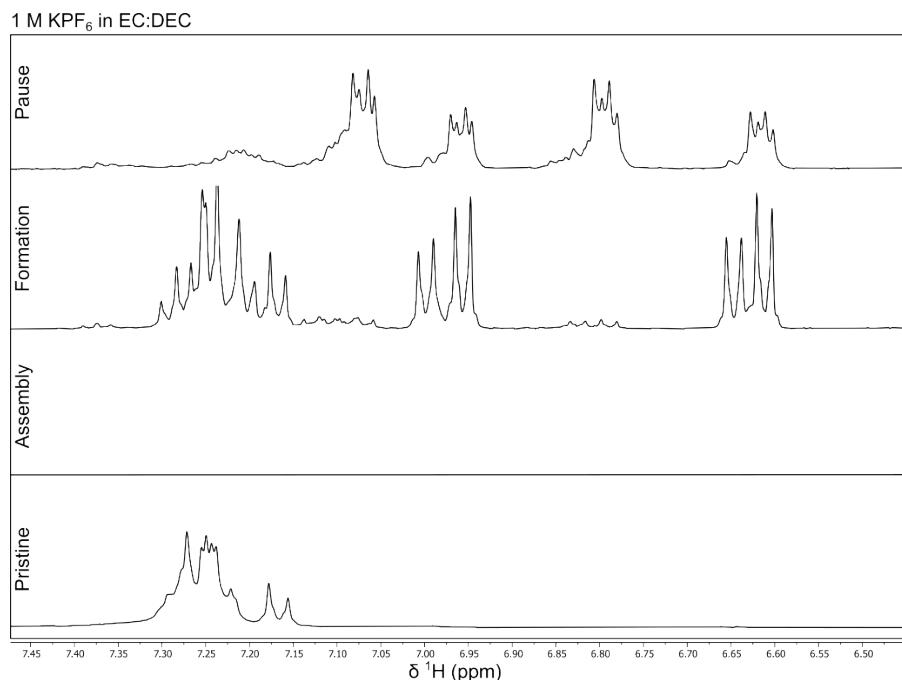
Sample	Site	Shift (ppm)	Integration normalized for each EC peak
S1 pristine	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.5579
	DEC (–CH <sub>3</sub> )	1.20	0.8369
S2 assembly	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.2264
	DEC (–CH <sub>3</sub> )	1.20	0.3414
S3 formation	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.2764
	DEC (–CH <sub>3</sub> )	1.20	0.4241
S4 50 h pause	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.2837
	DEC (–CH <sub>3</sub> )	1.20	0.4538

**Table S2**  $^1\text{H}$ -NMR solvent peaks and their integration values normalized for each EC peak in the K-system.

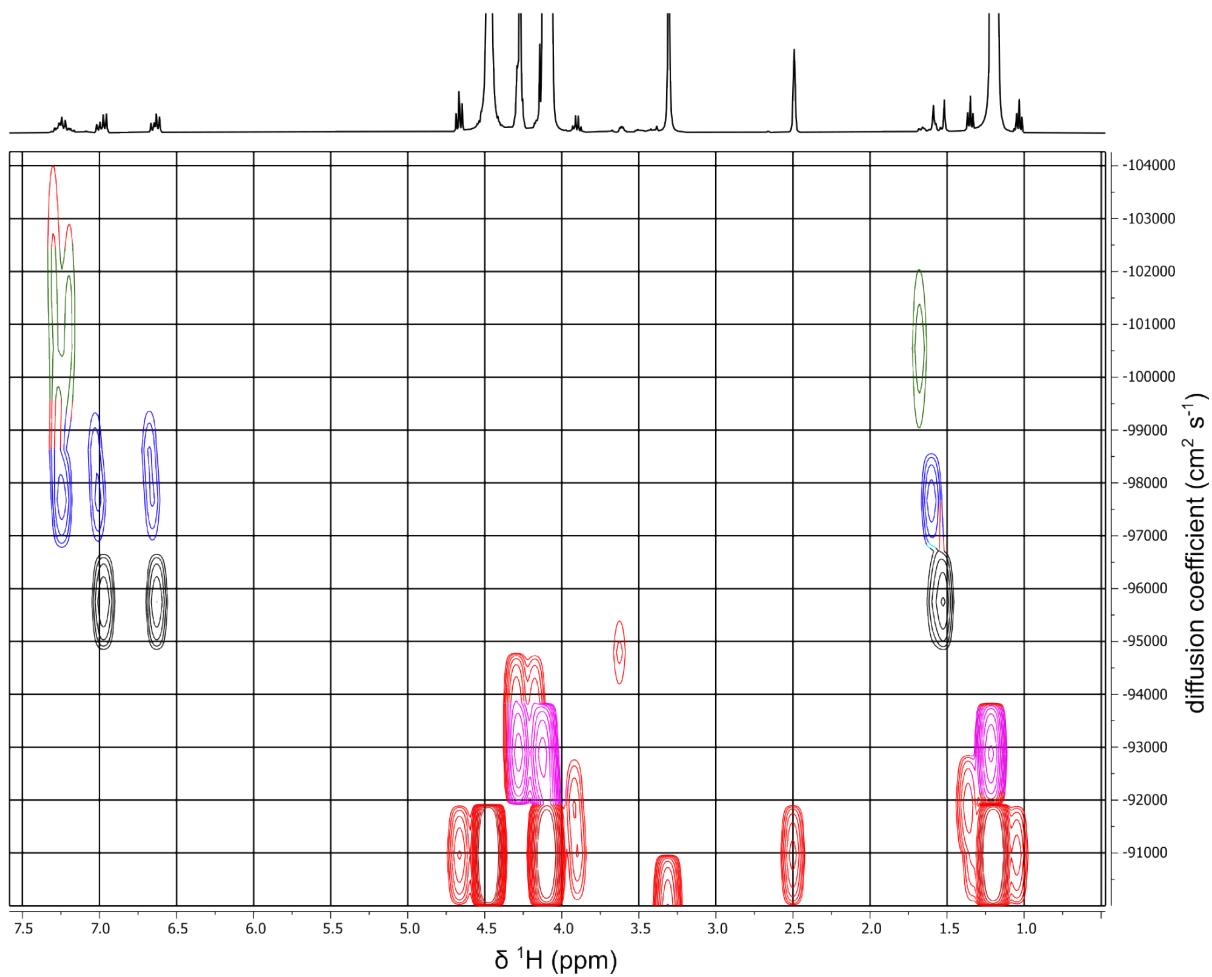
Sample	Site	Shift (ppm)	Intensity
S1 pristine	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.4862
	DEC (–CH <sub>3</sub> )	1.20	0.7341
S2 assembly	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.2327
	DEC (–CH <sub>3</sub> )	1.20	0.3577
S3 formation	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.3912
	DEC (–CH <sub>3</sub> )	1.20	0.5922
S4 50 h pause	EC	4.48	1
	DEC (–CH <sub>2</sub> –)	4.10	0.3057
	DEC (–CH <sub>3</sub> )	1.20	0.4622



**Figure S1** Qualitative analysis of the EC and DEC peaks in the four different states of 1 M  $\text{NaPF}_6$  or 1 M  $\text{KP}_6$  dissolved in EC:DEC (1:1). The y-axis shows the mole ratio of EC in the solvent mixture in percent. The values are calculated based on the  $-\text{CH}_2$  peak integration of DEC and the EC peak integration in the  $^1\text{H}$  NMR spectra.

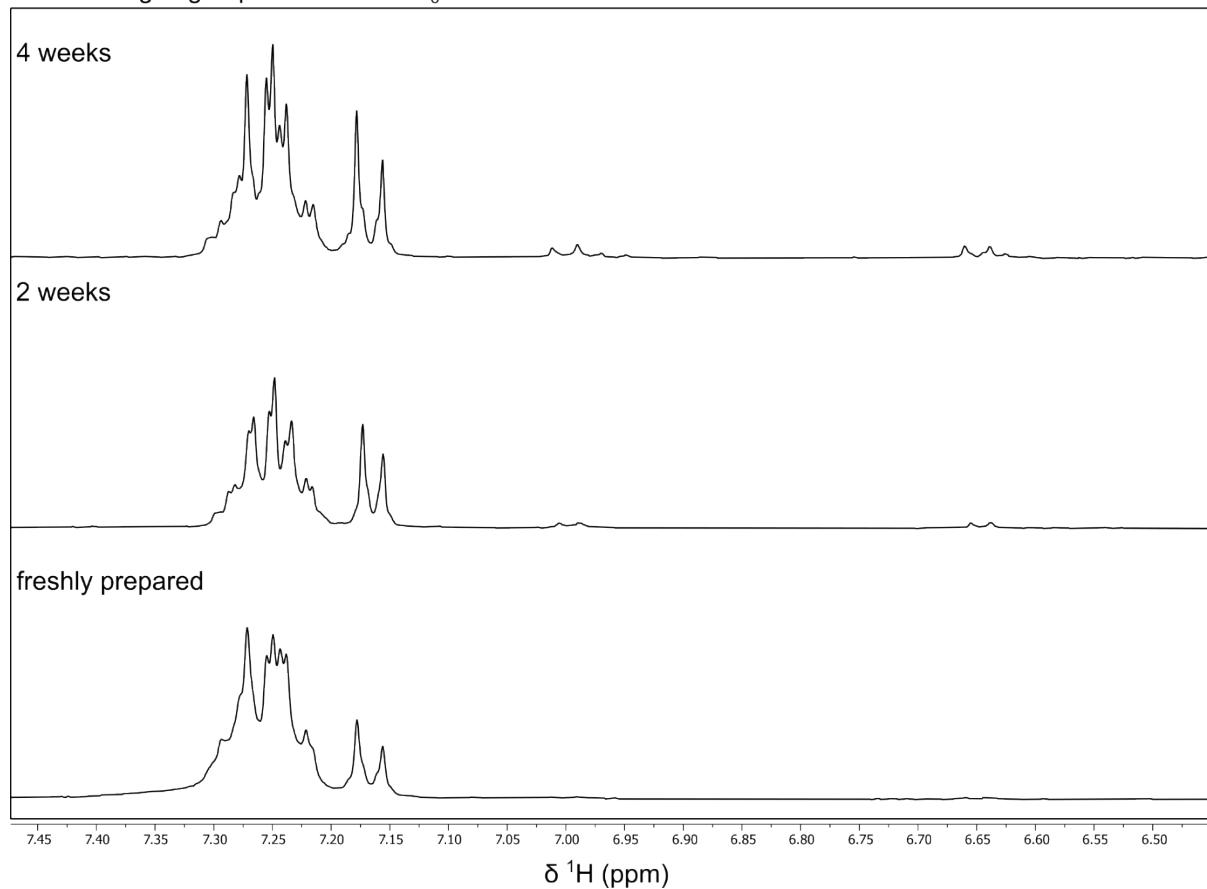


**Figure S2** There are impurities present in the 1 M  $\text{KPF}_6$  EC:DEC electrolyte. These impurities react with the cell components and form different kind of degradation products after the SEI formation and the pause. It is not clear what these species are.



**Figure S3** Diffusion ordered spectroscopy of the SEI formed 1 M  $\text{KPF}_6$  in EC:DEC cell. Green, blue and black highlighted peaks indicate that the impurity peaks at high chemical shifts (7.3-6.5) belong to three different species that also have protons with a low chemical shift.

Calendar ageing of pristine 1 M KPF<sub>6</sub> in EC:DEC



**Figure S4** <sup>1</sup>H-NMR of calendar aged electrolyte vs pristine 1 M KPF<sub>6</sub> EC:DEC solution. The multiplet at 7.25 ppm is also observed in the formation and pause cell (Figure S2). There are additional minor peaks appearing after two weeks at 7 and 6.65 ppm. These peaks are also observed in the other cells (Figure S3).

## References:

- (1) Ye, Z.; Hijazi, H.; Black, W.; Azam, S.; Dahn, J. R.; Metzger, M. Impact of Salts and Linear Carbonates on the Performance of Layered Oxide/Hard Carbon Sodium-Ion Pouch Cells with Alkyl Carbonate Electrolytes. *J. Electrochem. Soc.* **2024**, *171* (4), 040522. <https://doi.org/10.1149/1945-7111/ad3b73>.
- (2) Beda, A.; Vaulot, C.; Rabuel, F.; Morcrette, M.; Ghimbeu, C. M. The Role of Specific and Active Surface Areas in Optimizing Hard Carbon Irreversible Capacity Loss in Sodium Ion Batteries. *Energy Adv.* **2022**, *1* (4), 185–190. <https://doi.org/10.1039/D2YA00004K>.