Supporting information for

Anodic Dissolution of Aluminum in Non-Aqueous Electrolyte Solutions for Sodium-ion Batteries

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Materials:

1-methoxy-2-(2-methoxyethoxy)ethane (Diglyme) 99.5 % and triethyl phosphate (TEP) ≥99.8 % were purchased from Merck. Battery grade propylene carbonate (PC), ethylene carbonate (EC), and diethyl carbonate (DEC) were purchased from Gotion. Sodium hexafluorophosphate was purchased from Fluorochem, lithium bis(fluorosulfonyl)imide (NaFSI) 99.9 % from Solvionic, and sodium bis(oxalato)borate (NaBOB) was synthesized in-house as described previously.[1] All the solvents were dried using molecular sieves and filtered before use. High mass loading, low vacancy, Prussian white (12.2 ± 0.2 mg/cm^2) electrodes were obtained from Altris AB. These were then electrochemically charged to a potential corresponding to 3.3 V vs. Na$^+$/Na, after which they were referred to as Prussian blue electrodes. The aluminum foil was purchased from Goodfellow. The thickness of the foil was ~37 μm.

Preparation of reference electrodes:

The reference and counter electrodes were prepared by charging them against hard carbon electrodes in pouch cells to a potential corresponding to 3.3 V vs. Na$^+$/Na. The electrolyte solution used in this charging corresponded to the system in which these electrodes were later used. For example, the reference and counter electrodes used in the cells containing 1.00 m NaFSI in TEP were charged in 1.00 m NaFSI in TEP.

Electrochemical measurements:

As stated in the main text, all electrochemical measurements were performed using a three-electrode setup. Both the reference and counter electrodes were Prussian blue electrodes charged to 3.3 V vs. Na$^+$/Na. These electrodes were placed in polypropylene tubes, and contacted to aluminum strips, acting as current collectors. Glass fiber was placed at the end of the tubes to prevent Prussian blue particles from contaminating the working electrode. The reference and counter electrode were submersed directly in the cell solution; minimizing any liquid junctions. Each electrochemical experiment such as cyclic voltammetry and chronoamperometry was performed in a cell with a pristine aluminum working electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed at the open circuit potential (OCP) (Table S1) before and after each cyclic voltammetry and chronoamperometry experiment. The effect of reusing electrolyte solutions between measurements was evaluated for each electrolyte solution and electrochemical procedure. As a result, some experiments were performed in electrolyte solutions which had already been exposed to previous tests. For experiments resulting in evident anodic dissolution, the electrolyte solution was not reused.

The reference and counter electrodes were largely reused between the measurements. The potential of the reference electrodes was monitored between these measurements by checking that the potential was consistent against a fresh aluminum electrode immersed in an electrolyte solution that the reference electrode was intended to be used with. If the potential of the reference electrode was in question, the potential of the reference against metallic sodium was estimated. This was done by plating and stripping sodium-metal on aluminum, using the same type of electrolyte solution that the reference electrode was originally prepared in. Ideally, the onsets for the plating and stripping currents would appear around -3.3 V for an uncompromised Prussian blue reference electrode. However, underpotential deposition, or a general asymmetry in the overpotential for the plating and stripping sometimes complicated this assessment method. Solutions that had been in contact with metallic sodium were not reused in further experiments. In cases where the plating and stripping did not provide reassurance, replicates of previous experiments were performed. If a reference or counter electrode was deemed compromised, a new electrode was produced as a replacement. All the electrochemical measurements were performed in an argon filled glove box using a Biologic SP-240 potentiostat and an Autolab PGSTAT30.

XPS measurements:

X-ray Photoelectron Spectroscopy (XPS) was measured on aluminum working electrodes. These had prior the XPS-analysis undergone a chronoamperometric procedure initialized by a 10 min voltage step at 3.3 V vs. Na^+/Na, followed by a 5.3 V vs. Na^+/Na for 4 h, which ended at a 1 h relaxation at 3.3 V vs. Na^+/Na. After the electrochemical treatment, the solution above each sample was homogoniced by delicate konvection. The workingelectrode was thereafter extracted and washed using anhydrous mathanol. The masurements were conducted on a Kratos Axis supra+ instrument. During the measurement the samples were grounded against the instrument.

ICP-OES:

Inductively coupled plasma optical emission spectroscopy (ICP-OES), were performed on the electrolyte solutions used for the XPS sample preperation. The solutions were homogoniced before extractions form the cells. These solutions were thereafter sent to a company (Medac Ltd in United Kingdom) who performed the digestion and ICP-OES measurements. Density was determined for the 1.00 mol/kg NaFSI in TEP using a DMA-4100 density meter.
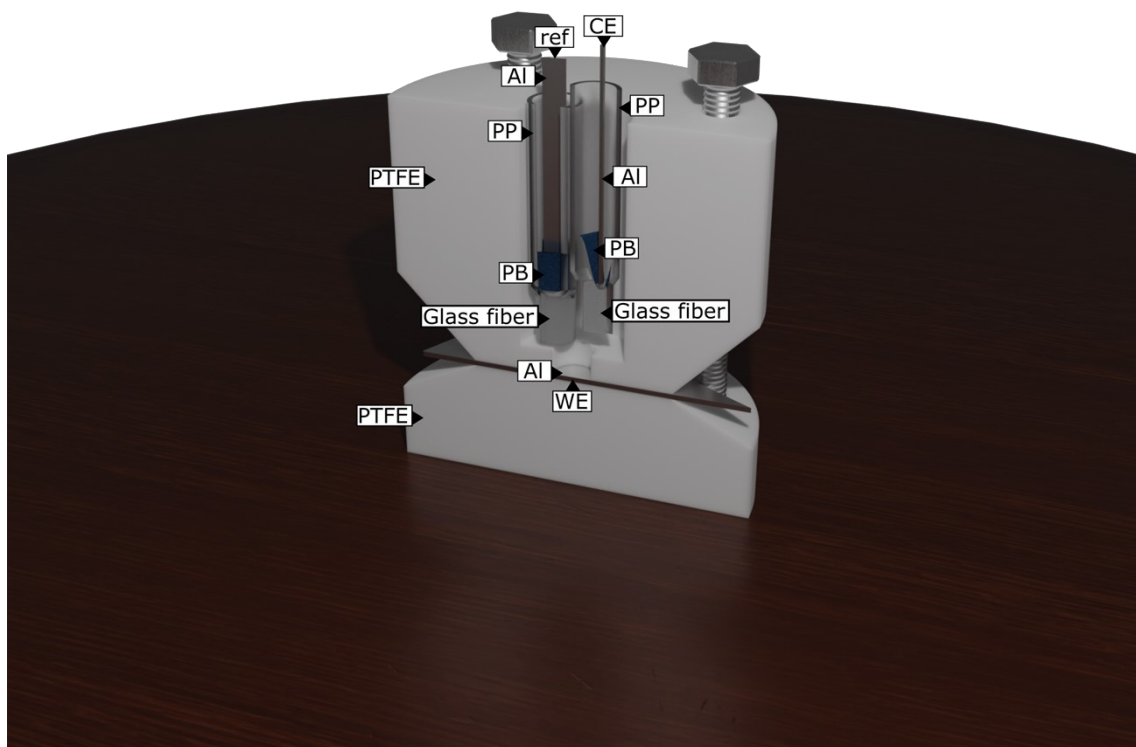
Figure S1: A schematic cross-section of the cell used in all the electrochemical experiments. The cell contained separate Prussian blue electrodes charged to 3.3 V vs Na^+/Na as reference (ref) and counter (CE) electrodes. These were contacted by aluminum current collectors and contained in polypropylene (PP) tubes. Glass fiber was used to prevent Prussian blue particles in the reference and counter electrodes from contaminating the working electrode.

Table S1: The average OCP values and standard deviations (based on 5 samples) for the pristine aluminum vs. Na$^+$/Na in each electrolyte solution

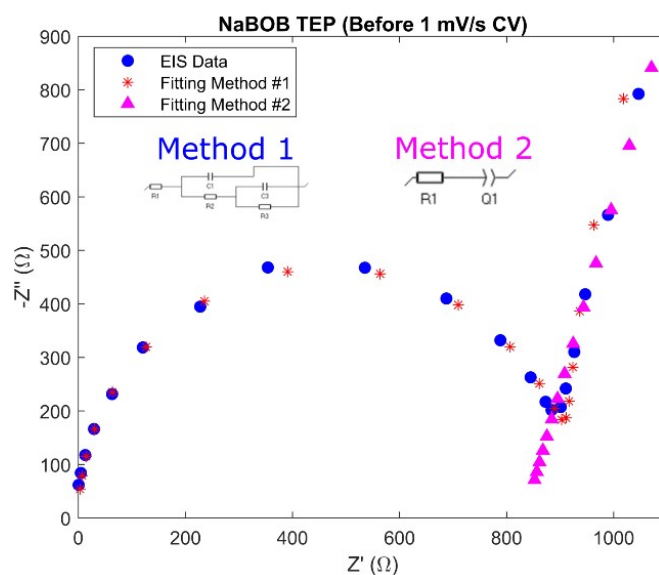| Electrolyte solution	Average value for OCP (V vs. Na$^+$/Na)	Standard deviation for OCP (V vs. Na$^+$/Na)
0.284 m NaBOB in TEP	2.05	0.08
1.00 m NaFSI in PC	2.22	0.05
1.00 m NaFSI in TEP	2.10	0.06
1.00 m NaPF$_6$ in EC:DEC	2.08	0.05
1.00 m NaPF$_6$ in Diglyme	2.07	0.06
1.00 m NaPF$_6$ in TEP	2.19	0.11

Figure S2: An impedance spectrum recorded between 1 MHz and 700 Hz for a cell containing the NaBOB in TEP electrolyte solution, which was later used to record a 1 mV/s CV. This spectrum displays the typical appearance for the EIS response of cells before chronoamperometry or cyclic voltammetry was conducted. Two fitting methods were used to evaluate the EIS results. The resistance values obtained form "Method 2" is shown as a descriptor in Table S2.

Table S2: Ohmic resistances evaluated from the impedance measurements on each cell before performing each cyclic voltammetry experiment. The resistance values were evaluated as *R1* according to "Method 2" shown in Figure S2.

| Electrolyte solution	Scan rate (mV/s)	Ohmic resistance (Ω)
0.284 m NaBOB in TEP	1	830
0.284 m NaBOB in TEP	10	810
0.284 m NaBOB in TEP	50	810
0.284 m NaBOB in TEP	100	840
0.284 m NaBOB in TEP	1000	810
1.00 m NaFSI in PC	1	400
1.00 m NaFSI in PC	10	380
1.00 m NaFSI in PC	50	500
1.00 m NaFSI in PC	100	380
1.00 m NaFSI in PC	1000	390
1.00 m NaFSI in TEP	1	460
1.00 m NaFSI in TEP	10	460
1.00 m NaFSI in TEP	50	410
1.00 m NaFSI in TEP	100	470
1.00 m NaFSI in TEP	1000	480
1.00 m $NaPF_6$ in EC:DEC 1:1 vol	1	350
1.00 m $NaPF_6$ in EC:DEC 1:1 vol	10	370
1.00 m $NaPF_6$ in EC:DEC 1:1 vol	50	370
1.00 m $NaPF_6$ in EC:DEC 1:1 vol	100	360
1.00 m $NaPF_6$ in EC:DEC 1:1 vol	1000	350
1.00 m $NaPF_6$ in Diglyme	1	440
1.00 m $NaPF_6$ in Diglyme	10	430
1.00 m $NaPF_6$ in Diglyme	50	450
1.00 m $NaPF_6$ in Diglyme	100	440
1.00 m $NaPF_6$ in Diglyme	1000	450
1.00 m $NaPF_6$ in TEP	1	560
1.00 m $NaPF_6$ in TEP	10	660
1.00 m $NaPF_6$ in TEP	50	690
1.00 m $NaPF_6$ in TEP	100	690
1.00 m $NaPF_6$ in TEP	1000	630
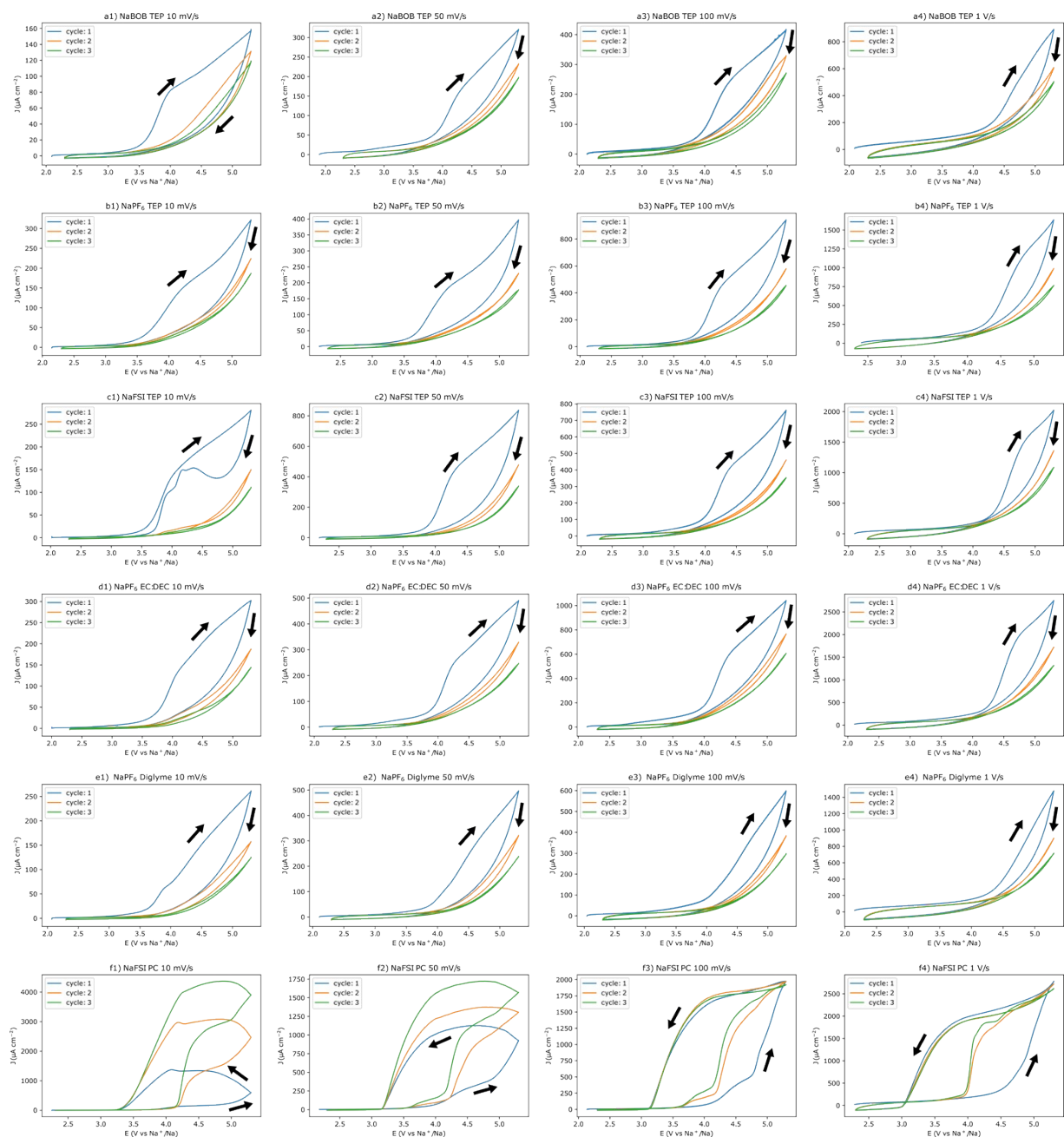
Figure S3: CVs recorded at different scan rates of 10 mV/s to 1 V/s (_1 to _4), for each electrolyte solution: a) NaBOB in TEP, b) NaPF$_6$ in TEP, c) NaFSI in TEP, d) NaPF$_6$ in EC:DEC, e) NaPF$_6$ in diglyme, and f) NaFSI in PC. The first three cycles are shown for each experiment. The arrows indicate the scan direction, which was consistent during the cycling.
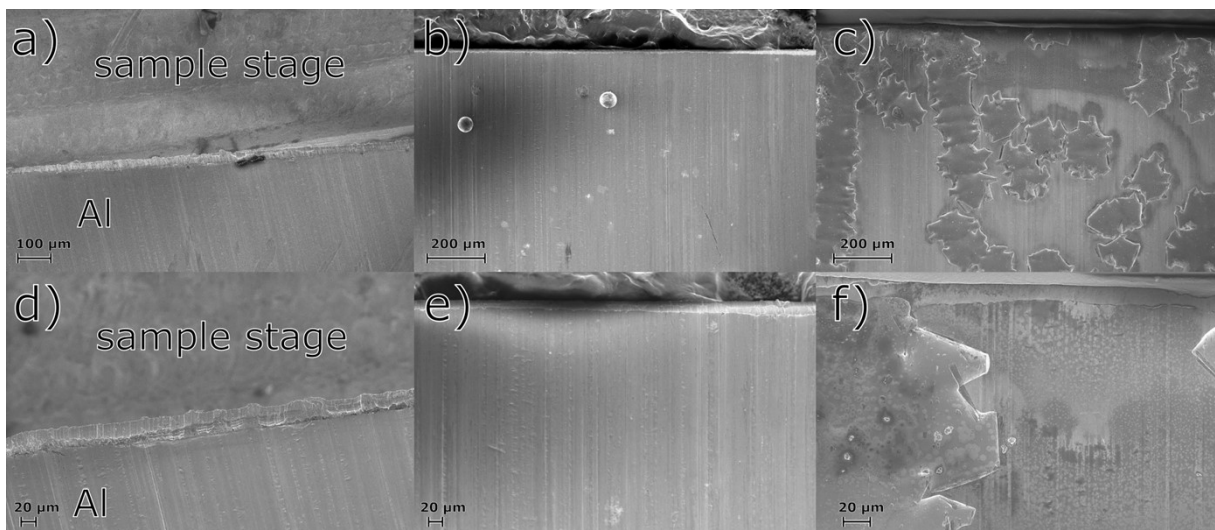
Figure S4: SEM images at different magnifications obtained for the pristine aluminum electrode in (a) and (d). The electrodes from the chronoamperometric experiment using NaFSI in PC is shown in (b) and (e), whereas the electrodes from the corresponding experiments using NaFSI in TEP are shown in (c) and (f).
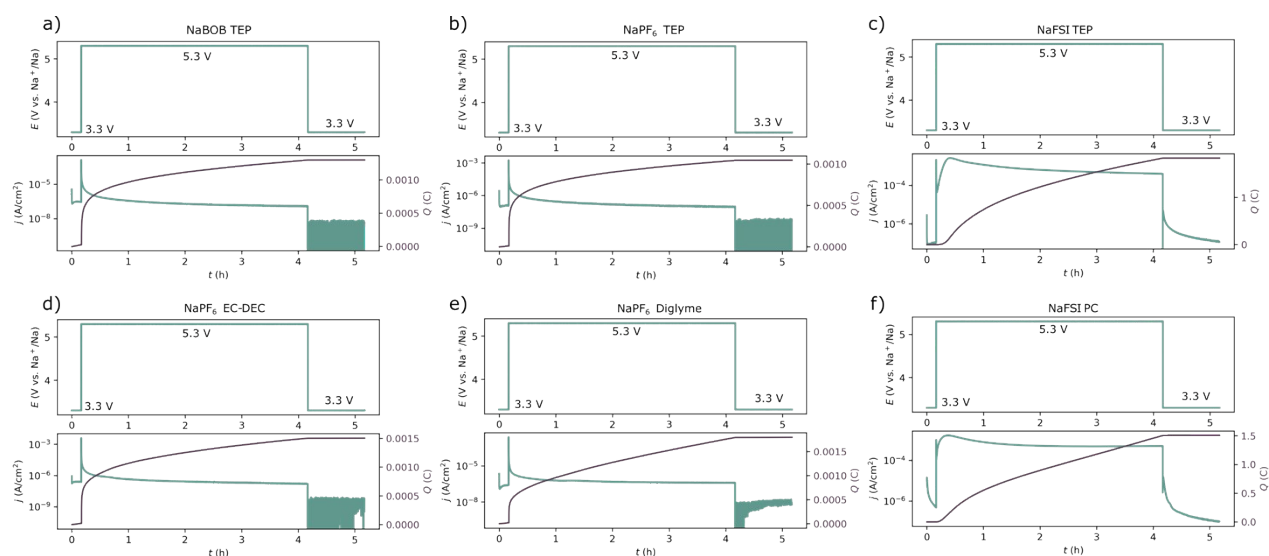

Figure S5: The chronoamperometric protocol and the resulting current-time curves for the experiment performed with an electrolyte solution composed of (a) 0.284 m NaBOB in TEP, (b) 1.00 m NaPF$_6$ in TEP, (c) 1.00 m NaFSI in TEP, (d) 1.00 m NaPF6 in EC:DEC, (e) 1.00 m NaPF6 in diglyme, and (f) 1.00 m NaFSI in PC. These measurements were the basis for the ICP-OES and XPS analysis.

Aluminum Foil

Al2p

C1s

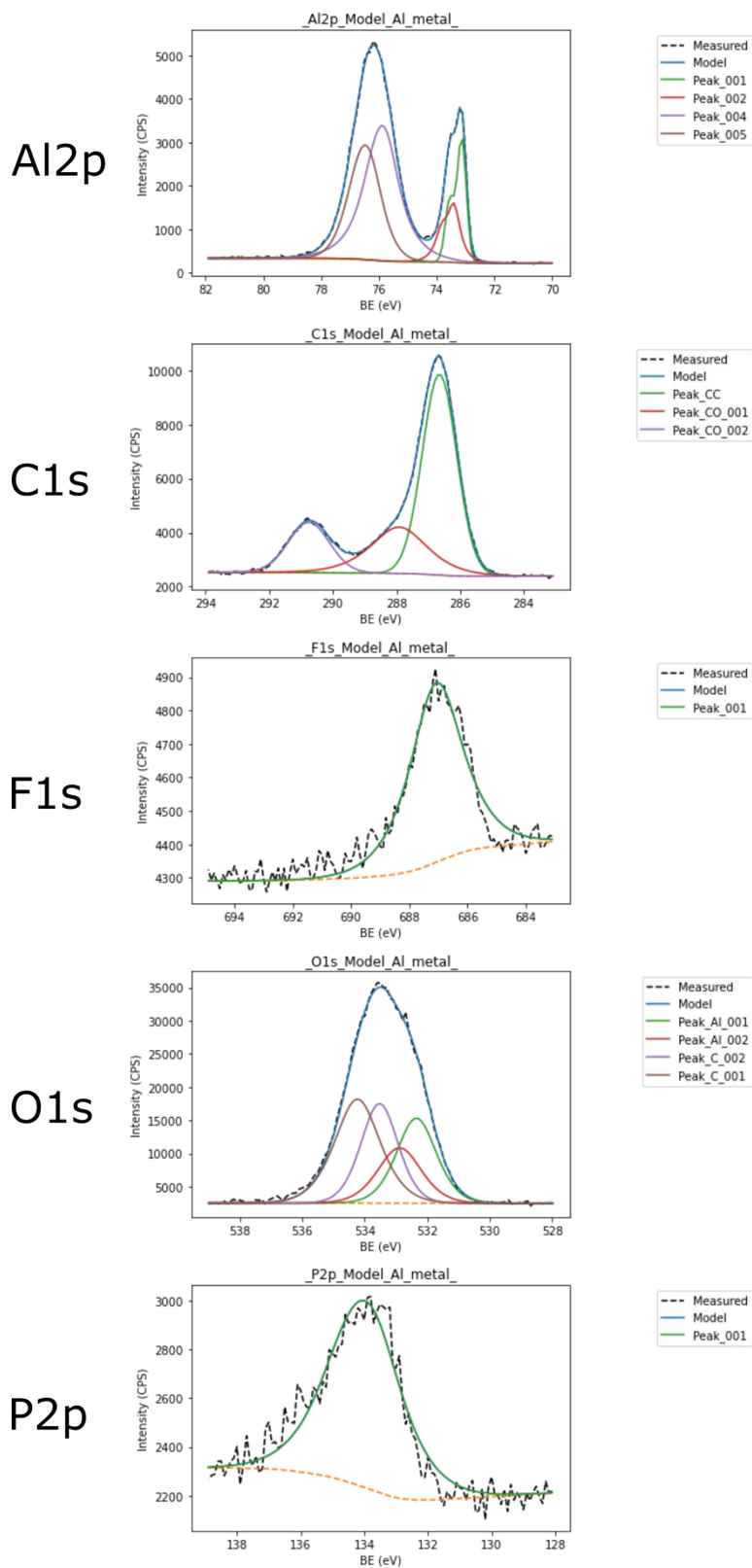**F1s**

O1s

P2p

Figure S6: XPS spectra and deconvolution of an aluminum foil. The fluorine and phosphorous is likely due to a cross contamination during the measurement. The spectra are shown without a specific energy calibration for the sample.
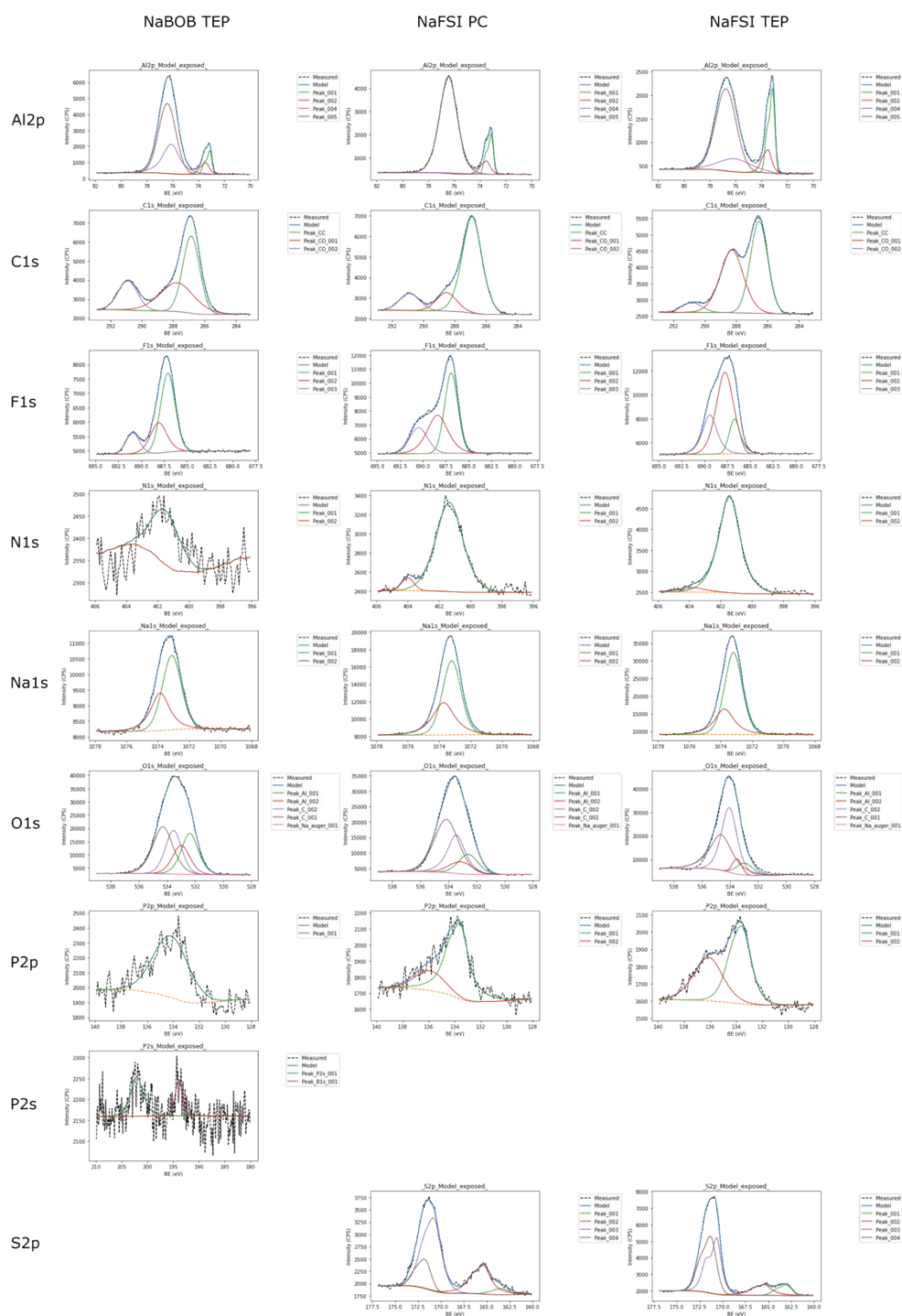
Figure S7: XPS spectra and deconvolution of aluminum used as working electrodes in contact with NaBOB in TEP, NaFSI in PC, and NaFSI in TEP, the preceding electrochemical measurements are shown in Figure S5. The fluorine in the NaBOB in TEP sample is likely due to a cross contamination during the measurement. The spectra are shown without a specific energy calibration for the sample. The figure is arranged to show each sample as a column and display individual element bands as rows.

Figure S8: XPS spectra and deconvolution of aluminum used as working electrodes in contact with NaPF$_6$ in EC:DEC, NaPF$_6$ in Diglyme, and NaPF$_6$ in TEP, the preceding electrochemical measurements are shown in Figure S5. The spectra are shown without a specific energy calibration for the sample. The figure is arranged to show each sample as a column and display individual element bands as rows.
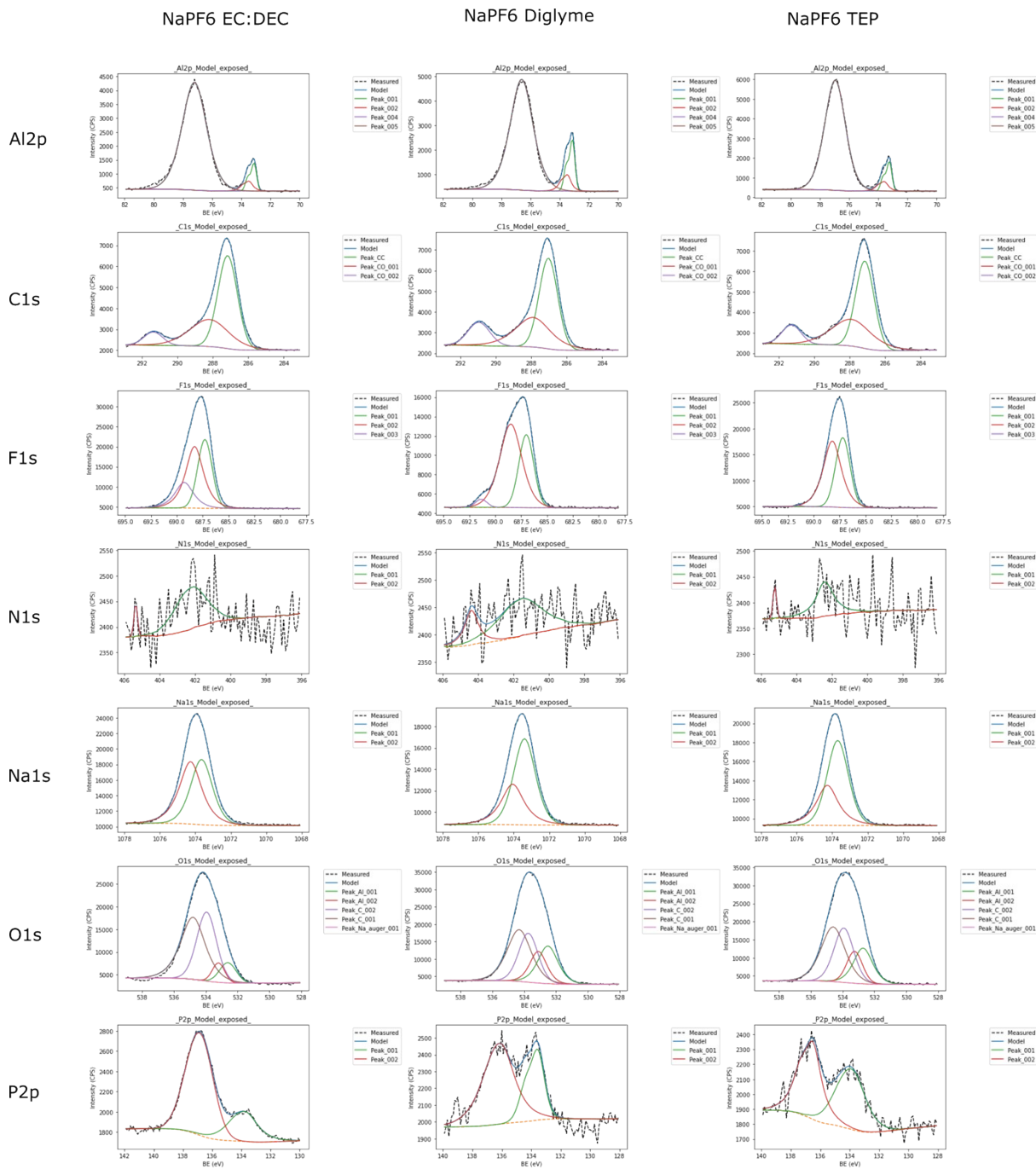
Note S1:

EIS measurements were performed at OCP (Table S1) before each cyclic voltammetry and chronoamperometry experiment. This was important since an inconsistent arrangement of the electrodes in the cell or the use of unrepresentative aluminum working electrodes may affect the reproducibility. In all the experiments, the reference electrodes were placed between the working and counter electrodes. Furthermore, the reference electrode was placed as close to the working electrode as possible without causing interference. An improper arrangement would show up in the EIS measurements, where the general shapes were compared between each measurement. The fitted resistances (Figure 2S, method 2) are presented as a descriptor in Table S2. It should be noted that using these resistances for compensating for the ohmic drop between the working and reference electrodes does not alter the results significantly. The OCP values were checked for consistency between each measurement; a variation of about 0.1 V for a given electrolyte solution was deemed acceptable.

Note S2:

Regarding the accuracy of the recorded potentials using a Prussian blue refence electrode, it must be highlighted that the Prussian blue reference electrodes seemed to spontaneously react in conjunction with the anodic dissolution of aluminum at the working electrode. In cases where severe anodic aluminum dissolution had taken place, the subsequent control of the potential of the reference electrode revealed that the potential of the reference electrode had changed from 3.3 V vs. Na^+/Na to 3.1–2.9 V vs. Na^+/Na. This was the case for the cells displayed in Figures 3c1 and f1. This means that there is some uncertainty in the potentials recorded after the potential steps where the cells started displaying evidence of anodic aluminum dissolution. A general sensitivity to redox active species in an electrolyte solution is one of the drawbacks of using intercalation driven electrodes as the reference electrode as has been observed in other systems as well.[2] Nevertheless, intercalation materials are one of the most viable types of reference electrodes for use with non-aqueous sodium-based electrolyte solutions that spontaneously react with metallic sodium. However, this highlights the importance of verifying the potential of an intercalation type reference electrode after it has been used in an experiment.

Note S3:

Apart from affecting the onset potential for anodic aluminum dissolution, the solvent also appeared to affect the morphology of the remaining surface. The pristine aluminum foil is shown as a reference in Figure S4a and d. For NaFSI in PC, the anodic dissolution resulted in the emergence of hemispherical pits (Figure S4b), or roughened spots (Figure S4e). In contrast, the use of NaFSI in TEP seemed to cause a more dispersive exfoliation with sharp edges (Figure S4c and f). The difference in morphology of the corroded areas and the difference in electrochemical response suggest that the nature of the solvent affected the dissolution mechanism.

References

1   L. O. S. Colbin *et al.*, "A Halogen-Free and Flame-Retardant Sodium Electrolyte Compatible with Hard Carbon Anodes," *Adv. Mater. Interfaces*, vol. 8, no. 23, pp. 1–10, 2021, doi: 10.1002/admi.202101135.

2   R. Mogensen, S. Colbin, and R. Younesi, "An Attempt to Formulate Non-Carbonate Electrolytes for Sodium-Ion Batteries," *Batter. Supercaps*, vol. 4, no. 5, pp. 791–814, 2021, doi: 10.1002/batt.202000252.