Sustainable and Safe anode-free Na Battery

H2020-M-ERA.Net -3 Call 2021

Start date of the project: 01/09/2022

Duration: 36 months

Deliverable D6.1

Report on summary of electrochemical measurements with different electrolytes

Project partners

LOGO	Partner full name	Acronym
CSIC	Agencia Estatal Consejo Superior de Investigaciones Científicas	CSIC
JÜLICH Forschungszentrum	Forschungszentrum Jülich GmbH	FZJ
ALTRIS	Altris AB	Altris
DTU Danmarks Tekniske Universitet	Danmarks Tekniske Universitet	DTU
PHASETREE	PhaseTree	PT

	Uppsala University	UU
	ACCUREC Recycling GMBH	ACC

Deliverable Name: Report on summary of electrochemical measurements with different electrolytes

Led by: UU

Participant partners: FZJ, CSIC

Date	Version	Author	Institution	Comments*
15/11/2023	1	Aram Hall	UU	creation
2023-01-16	1	Simon Colbin	UU	Additions
2024-02-28	1	Aram Hall	UU	Additions

* Creation, modification, final version for evaluation, revised version following evaluation, final

TYPE	Disseminati on Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	2 / 18

List of Acronyms

Acronym	Description
PC	propylene carbonate
DMC	dimethyl carbonate
G2	diethylene glycol dimethyl ether
TEP	triethyl phosphate
EC	ethylene carbonate
LiFSI	lithium bis(fluorosulfonyl)imide
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide
SIB	sodium ion battery
NaBOB	sodium bis(oxalato)borate
CV	cyclic voltammetry
CC-Al	carbon-coated Al
SS	stainless-steel

Content

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	3 / 18

Figure Index

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	4 / 18

Table Index

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	5 / 18

Introduction

This report details a summary of the results of preliminary electrochemical testing, focussing in particular on comparing the electrochemical testing of different electrolyte solutions. These results range from physical characterisation (preliminary determination of candidate solvents and salts, conductivity measurements using cosolvent mixtures etc), compatibility testing of these solvents with the membranes created in WP3, and early-stage electrochemical testing in 'anodeless' cell configurations.

This report will act as the first stage of a two-part report. The second stage, 'D6.2 - Report on progress of electrochemical measurements with different electrolytes' will be delivered at the end of the project. This report is delivered along with 'Ms6.1 Optimized protocol of electrochemical cycling of full-cells', for which optimised cycling protocols are included within this report.

Membrane-Solvent Compatibility

In order to ensure that membranes produced in WP 3 are suitable for use in cells in the SuSaNa project, solvent compatibility tests were conducted. Four base solvents were used: propylene carbonate (PC), dimethyl carbonate (DMC), diethylene glycol dimethyl ether (G2) and triethyl phosphate (TEP). These were selected as representative candidates from the cyclic carbonates, linear carbonates, glymes and organophosphates. Some variability in the compatibility will certainly exist within these classes (i.e. one should not necessarily assume that for example PC and ethylene carbonate (EC) will produce comparable results) but these results are presented as an early indication of compatibility.

With these solvents, 4 membranes were tested: PC-PEO (85:15), PSF-PEO 80, PC 90, PCA/Cellulose + PEO (90:10). SEM images of the membranes appear in Figure 1. The compositions of these membranes are detailed below in Table 1. Membrane integrity was assessed after 6 days, 15 days, and 6 weeks. The results are presented in Table 2.

The membrane composition which best endures the solvents, particularly G2, is the one prepared with PLA, cellulose and PEO. The CSIC group has chosen PLA-based membranes as the target for membrane optimization as regards composition, pore size and pore morphology. Optimised membranes will be tested in Uppsala University during April and May 2024 during the stage of the PhD student from CSIC, Ángela Campo.

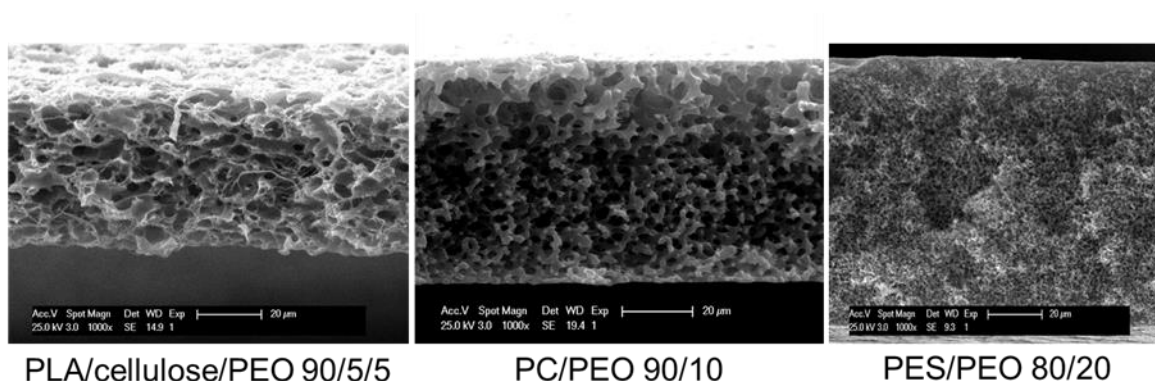PLA/cellulose/PEO 90/5/5   PC/PEO 90/10   PES/PEO 80/20

FIGURE 1 SEM IMAGES OF THE MEMBRANES IN TABLE 1.

TABLE 1: DETAILS OF TESTED MEMBRANES

Membrane Name	Composition (wt.%)	Chemical Structure
PC/PEO	85/15	
PC/PEO	90/10	
PES/PEO	80/20	
PLA/Cellulose/ PEO	90/5/5	

TABLE 2: MEMBRANE COMPATIBILITY

Compatibility (observed 6 weeks)				
	PC	**DMC**	**G2**	**TEP**
PC-PEO (85:15)	Good	Good	Marginal	Poor
PSF-PEO 80	Good	Good	Fail	Fail
PC 90	Good	Fail	Marginal	Marginal
PCA/Cellulose + PEO (90:10)	Good	Good	Good	Good

Good – no observable damage after 6 weeks.

Marginal – some damage (specifically not disintegration) observed after 6 weeks.

Poor – no damage observed after 6 days, but failure at longer durations.

Fail – immediate or near immediate disintegration.

Electrochemical Measurements of Electrolytes

The electrochemical measurements here are split into 5 sections, focussing on: (i) anodic dissolution of aluminium current collectors in different electrolyte solutions, (ii) exchange current density measurements of sodium plating and stripping, (iii) physical properties reference electrolyte solution, (iv) 'anodeless' cell architecture current collector materials, and (v) optimised cycling protocols for full cell testing. The results from the first section on anodic dissolution of Al have been published in Energy Advances (Colbin et al, *Energy Adv.*, 2024, Advance Article). The results of the second and third section on exchange current density and physical properties of the reference electrolyte have been passed to WP5 for use in multiscale modelling. Working in the final two sections is in its infancy and it is undetermined if it will be published or only used internally in SuSaNa to guide further experiments.

3.1.   Anodic Dissolution of Aluminium Current Collectors

A problem in the pursuit of new electrolyte compositions is the possibility of anodic dissolution of the Al current collector on the positive electrode (also commonly termed corrosion, although such description, whilst helpful for a broad audience, is debatable). This phenomenon is for example well

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	8 / 18

established in the Li-ion battery field for many electrolyte compositions containing lithium bis(fluorosulfonyl)imide (LiFSI) or lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Relatively little however had been published on how such anodic dissolution of Al occurs in sodium ion batteries (SIBs), and in particular how and when such anodic dissolution occurred when TEP is employed as the electrolyte solvent (TEP being pertinent to SuSaNa as a promising non-flammable, potentially low toxicity alternative to carbonate solvents). It was hypothesised previously that a lack of anodic dissolution in cells using sodium bis(oxalato)borate (NaBOB) in TEP electrolyte evidenced passivation of the Al on the positive current collector, but it was unclear if such a passivation was due to the NaBOB, the TEP, or the combination of the two. As such this study further aimed to unravel this mystery.

Given the full results are published (Colbin, Hall, Etman, Buckel, Nyholm and Younesi, 'Anodic dissolution of aluminium in non-aqueous electrolyte solutions for sodium-ion batteries', Energy Adv., 2024, doi: https://doi.org/10.1039/D3YA00233K) an abridged version is presented here. Six electrolyte solutions were evaluated: 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 1 : 1 vol; e) 1.00 m NaPF$_6$ in diglyme; f) 1.00 m NaFSI in PC. From the cyclic voltammetry (CV) behaviour of the first and second cycle (*Figure 2*), it can be seen that NaBOB in TEP and NaPF$_6$ in TEP, Diglyme, or EC:DEC (1:1) all show evidence of passivation up to 5 V vs Na$^+$/Na. In contrast, NaFSI in both TEP and PC showed evidence of anodic Al dissolution. Whilst this confirms that NaBOB is responsible for the observed passivation in NaBOB in TEP electrolyte, there is evidence that TEP retards anodic Al dissolution when NaFSI is used.
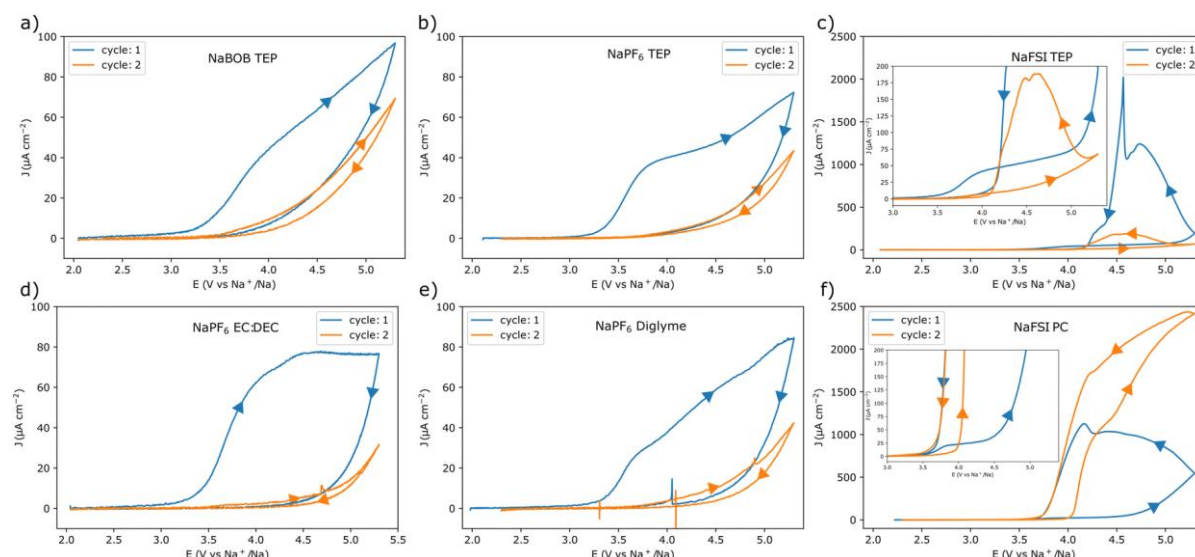
FIGURE 2 CYCLIC VOLTAMMETRY OF: A) 0.284 M NABOB IN TEP; B) 1.00 M NAPF$_6$ IN TEP; C) 1.00 M NAFSI IN TEP; D) 1.00 M NAPF6 IN EC : DEC 1 : 1 VOL; E) 1.00 M NAPF$_6$ IN DIGLYME; F) 1.00 M NAFSI IN PC. THE EXPERIMENT WAS PERFORMED AT SCAN RATE WAS 1 MV/S, IN A 3 ELECTRODE CONFIGURATION WITH PRUSSIAN

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	9 / 18

3.1.   Exchange Current Density

In order to more accurately model Na plating, WP 5 of the SuSaNa project undertakes to models Na plating on current collector surfaces. One key input in this is the exchange current density, which is taken from experimental measurement. Measurements were performed in an in-house designed beaker cell using a sodium counter, reference and working electrode, and 1 m $NaPF_6$ in diglyme electrolyte. The use of the diglyme based electrolyte is necessary in this case to avoid reactions between the solvent and the sodium, which occurs in a great many electrolyte solutions. Measurements at different temperatures of two replicate cells are shown in *Figure 3*. The current results suggest that temperature dependence of the exchange current density is well captured by the Butler-Volmer equation.

TYPE	Dissemination Level	NAME	REFERENCE				PAGE
			Document ID	Edition/revision	DATE		
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023		10 / 18

Example Fit

Replicate 1

Replicate 2
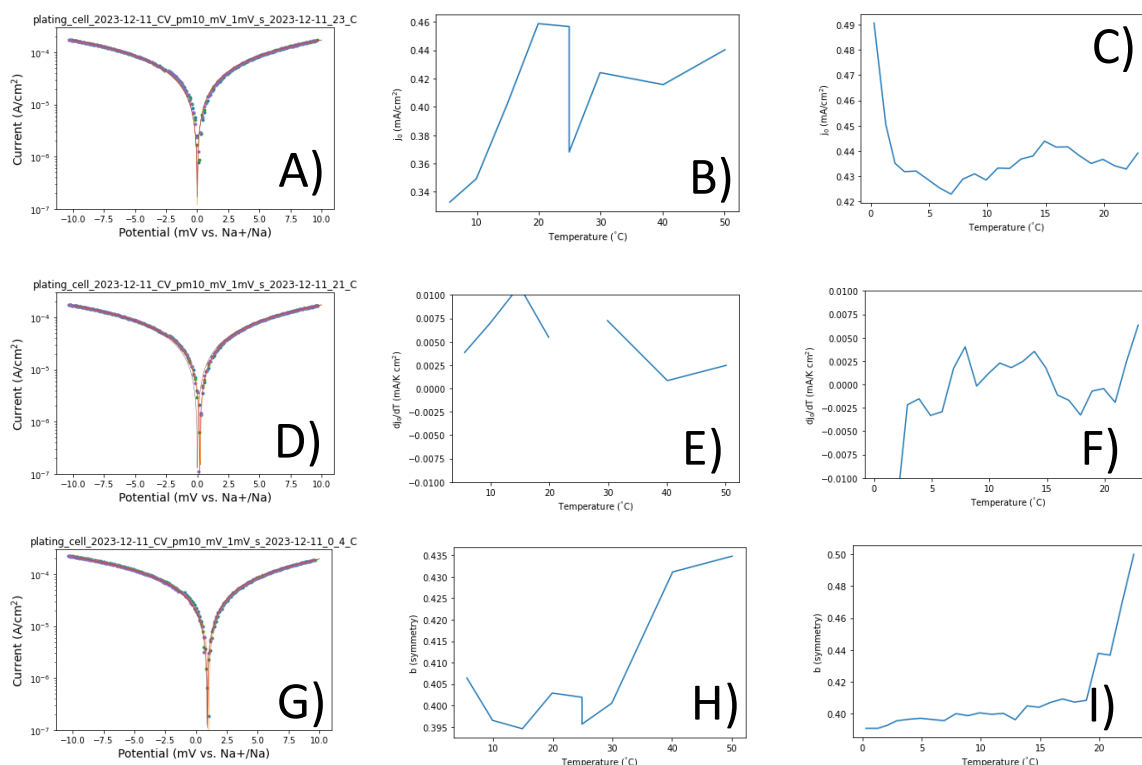
FIGURE 3 BUTLER-VOLMER FITS OF CYCLIC VOLTAMMETRY DATA AND DERIVED EXCHANGE CURRENT DENSITY AND ASYMMETRY AT DIFFERENT TEMPERATURES. THE FITS IN A, D AND E ARE FROM REPLICATE 2 AT 23°C, 21°C AND 4°C RESPECTIVELY. THE FITTED EXCHANGE CURRENT DENSITY IS SHOWN B AND C, DJ_0/DT IN E AND F, AND THE SYMMETRY TERM, 'B', IN H AND I.

3.1. Physical properties reference electrolyte solution

Both empirical calculations and more sophisticated simulations need physical parameters. Some relevant physical parameters were recorded on the reference electrolyte solution $NaPF_6$ in Diglyme. Namely: viscosity, density, and conductivity at different concentrations. In addition, these viscosities and densities were recorded at different temperatures (Table 3). These results will help when trying to model, or interpreted experiments involving, mass transport limited sodium plating in the reference solution.

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	11 / 18

TABLE 3: VISCOSITY, DENSITY, AND CONDUCTIVITY OF NaPF$_6$ IN DIGLYME AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration molal mol/ kg	conductivity mS/cm (temperature °C)	density g/cm³ (10 °C)	density g/cm³ (15 °C)	density g/cm³ (20 °C)	density g/cm³ (25 °C)	density g/cm³ (30 °C)	density g/cm³ (40 °C)	density g/cm³ (50 °C)	viscosity mPas (10 °C)	viscosity mPas (15 °C)	viscosity mPas (20 °C)	viscosity mPas (25 °C)	viscosity mPas (30 °C)	viscosity mPas (40 °C)	viscosity mPas (50 °C)
0.01266	0.0420 (26.1)	0.9552	0.9502	0.9453	0.9403	0.9353	0.9253	0.9152	1.292	1.1819	1.0847	1.0003	0.926	0.8021	0.704
0.03464	0.123 (26.1)	0.9576	0.9527	0.9477	0.9428	0.9378	0.9278	0.9177	1.3207	1.2071	1.1073	1.0214	0.9454	0.8184	0.7185
0.09352	0.458 (26.2)	0.965	0.9601	0.9551	0.9501	0.9452	0.9352	0.925	1.4062	1.2834	1.1766	1.086	1.0036	0.8681	0.7598
0.5348	4.08 (27.2)	1.0154	1.0106	1.0056	1.0007	0.9958	0.9858	0.9758	2.2047	1.9849	1.7977	1.638	1.5011	1.281	1.1085
1.079	7.17 (27.2)	1.0721	1.0673	1.0624	1.0576	1.0527	1.0429	1.033	3.9101	3.4456	3.0601	2.7364	2.4635	2.0296	1.7021

3.2.   Anodeless Electrode Materials

In order to meet the aims of the SuSaNa project for a cell composed of a Prussian white cathode in an anodeless configuration (i.e. having an anode current collector onto which Na is plated and stripped), a suitable anode current collector is needed. Aluminium is commonly used as a current collector in sodium ion batteries, but is well known to be a difficult material to plate metals onto. Other materials, for example Au, are known to produce more conformal Na plating and reduce inhomogeneous Na '*dendrites*' (these growth patterns are not necessarily the same as dendrites in LIBs, but the term dendrite is used here for ease of understanding) but are prohibitively expensive.

As a starting point, Al foil was compared to carbon-coated Al foil (CC-Al) and stainless-steel (SS) plates as current collectors. These tests were performed in a Na||current collector configuration using 1 m $NaPF_6$ in diethylene glycol dimethyl ether and DreamWeaver Gold separator. A current density of 1 mA/cm^2 was applied for 2 h for each plating and stripping cycle. In line with expectations, the plating and stripping of Na on Al, shown in Figure 4, is poor and the cell shorts within 5 cycles. Such results were observed for all replicates (5 cells).
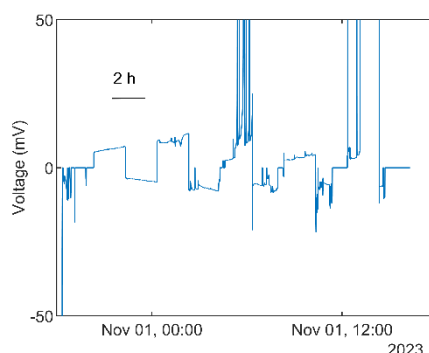

FIGURE 4 PLATING STRIPPING EXPERIMENT IN NA||AL CELL.

In contrast to plating and stripping Na from Al, plating and stripping onto CC-Al appeared to produce much improved stability. The plating and stripping potential (~10 mV) at the current density used was near the resolution limit of the cycling equipment, and these values make it difficult to discern whether the results are indicative of a stable short circuit (either due to separator puncture or *dendrites*) or desirable cycling. Results for a representative cell are shown in *Figure 5*, for which 100 cycles were reached before the test was ended. Plating and stripping of Na onto SS was observed to be similar to CC-Al, if slightly less stable (i.e. showing more voltage spikes during plating and stripping). It is unknown to what extent this stability is due to stack pressure and to what extent it's due to differences in the ease with which Na plating and stripping occurs. A representative cell is shown in *Figure 6*.
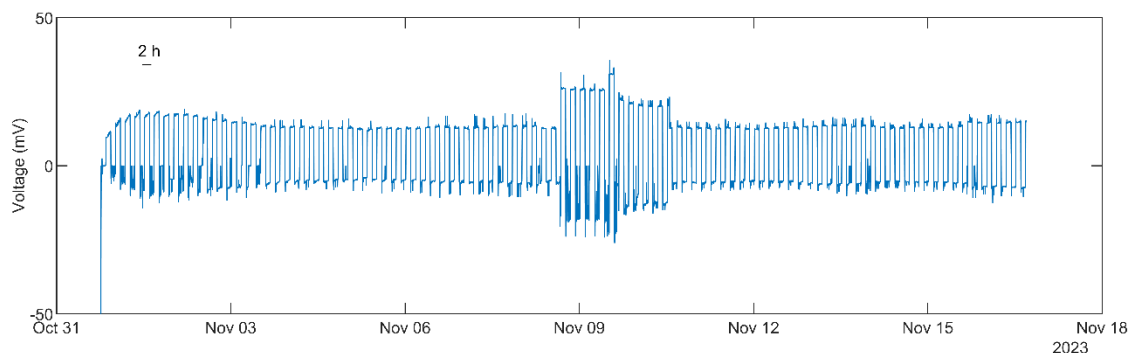
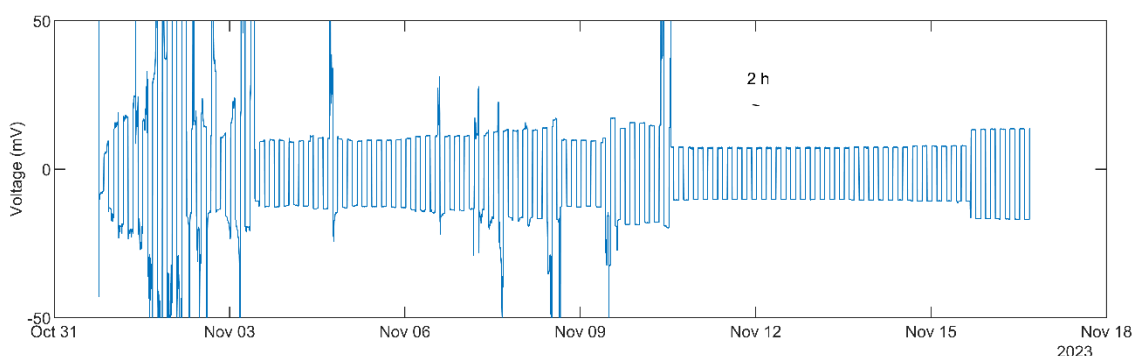*FIGURE 5 PLATING STRIPPING EXPERIMENT IN NA||CARBON-COATED AL CELL.*

FIGURE 6 PLATING STRIPPING EXPERIMENT IN NA||STAINLESS STEEL CELL.

3.3. Ms6.1 Optimized protocol of electrochemical cycling of full-cells

Following on from the initial testing of anodeless half cells, it was necessary as part of Ms6.1 to define optimized protocols for cycling full cells (i.e. PW||anodeless current collector). Standard cycling protocols are seen as necessary for the SuSaNa project in order to facilitate comparison of the results between the different partners. Such protocols may aid a systematic assessment of any changes done to a system according to whatever goal each partner sets out to achieve, or help in trouble shooting a system. However, due to the nature of plating sodium on a non-sodium substrate from a Prussian white material, a single standard protocol is not sufficient! UU has therefore proposed 3 different protocols to aid the assessment of anode-less sodium plating from Prussian white. These protocols do not include information about formation cycling. It would be unwise to recommend a general formation protocol since this will have a too large of an impact on

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	14 / 18

substrate, additives, and the general formulation of the electrolyte solution. If there is no interest in the formation, UU recommends performing the first 5 cycles at a half (or slower) of the cycling rate that is stated for each standard procedure, or alternatively start the regular protocol immediately from the first cycle.

The 3 protocols developed are described separately below, and for simplicity of communication are named as their intended functions within cell testing: Protocol 1: 'Be Normal'; Protocol 2: 'Be Nice'; and Protocol 3: 'Be Mean'.

Protocol 1: "Be normal"

The *Be normal* protocol aims to simulate a naïve cycling protocol. Here the cycling is performed as it would be for any regular battery cell. The parameters for this procedure are shown in Table 4, with the resulting cycling in Figure 7.

TABLE 4 DESCRIPTION OF PROTOCOL 1: "BE NORMAL"

Parameters for the Be normal cycling procedure	
Charge	
Cell potential cutoff	3.5 V
C-rate (based on Prussian white 150 mA/g)	0.2 C, or 30 mA/g
Discharge	
Cell potential cutoff	1 V
C-rate (based on cathode 150 mA/g)	0.2 C, or -30 mA/g

The benefit of the *Be normal* procedure is that any sodium inventory loss should be visible instantly, starting from the first discharge. It could also be considered a conventional, and "fair" cycling protocol.

The drawbacks are that it is hard to control of the potential of the anode. This could cause unwanted site reactions, e.g. oxidation of an SEI. Every cycle should also undergo a sodium seeding of the surface, which both leads to a peculiar overpotential, and potential loss of sodium inventory.

FIGURE 7: A PRUSSIAN WHITE CATHODE CYCLED, ACCORDING TO THE BE NORMAL PROTOCOL, AGAINST A CARBON COATED ALUMINIUM ANODE, USING A SODIUM REFERENCE ELECTRODE. THE FIRST CYCLE IS SHOWN. E_{CELL} IS THE CELL POTENTIAL, WHAT IS VISIBLE IN TWO-ELECTRODE CYCLING. E_1 AND E_2 ARE THE POTENTIALS OF THE PRUSSIAN WHITE CATHODE AND CARBON COATED ALUMINIUM/SODIUM ANODE RESPECTIVELY. THESE ELECTRODE POTENTIALS ARE SHOWN WITH RESPECT TO A SODIUM REFERENCE ELECTRODE.

Protocol 2: "Be Nice"

The *Be nice* procedure leverages the fact that Prussian white has two distinct redox processes, giving rise to two distinct plateaus. Here cycling is performed on Prussian white's upper plateau (actually sodium variant of Prussian blue cycled to Berlin green), which will result in a reservoir of plated sodium on the anode. The parameters for this procedure are shown in Table 5 and the resulting cycling curve in Figure 8.

TABLE 5 DESCRIPTION OF PROTOCOL 2: "BE NICE"

Parameters for the Be nice cycling procedure	
Charge	
Cell potential cutoff	3.5 V
C-rate (based on Prussian white 150 mA/g)	0.2 C, or 30 mA/g
Discharge	
Cell potential cutoff	3.1 V
C-rate (based on cathode 150 mA/g)	0.2 C, or -30 mA/g

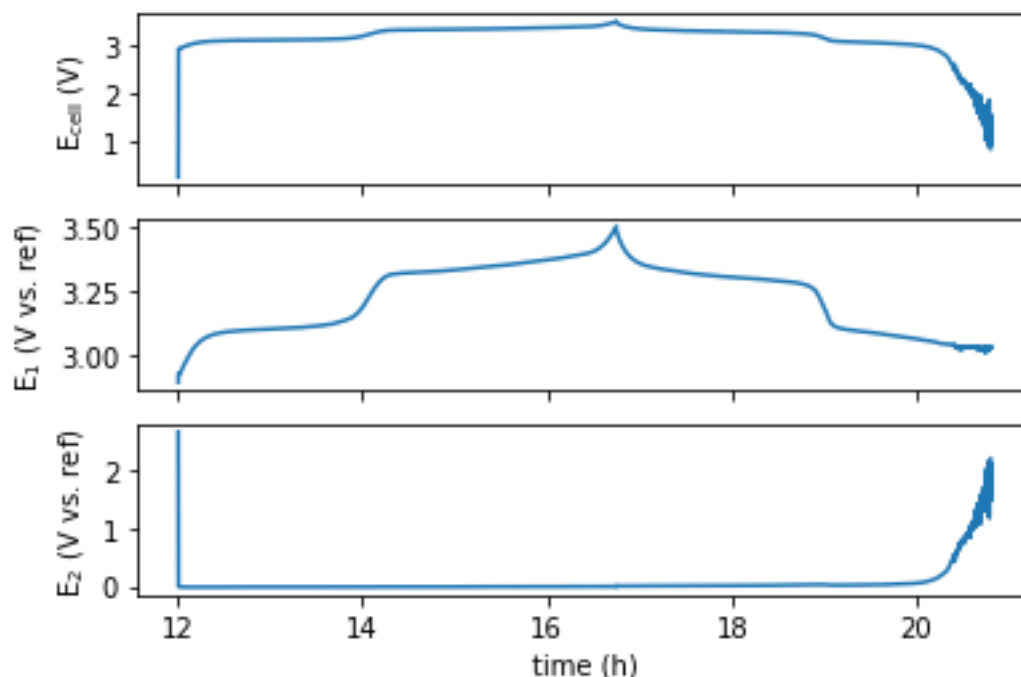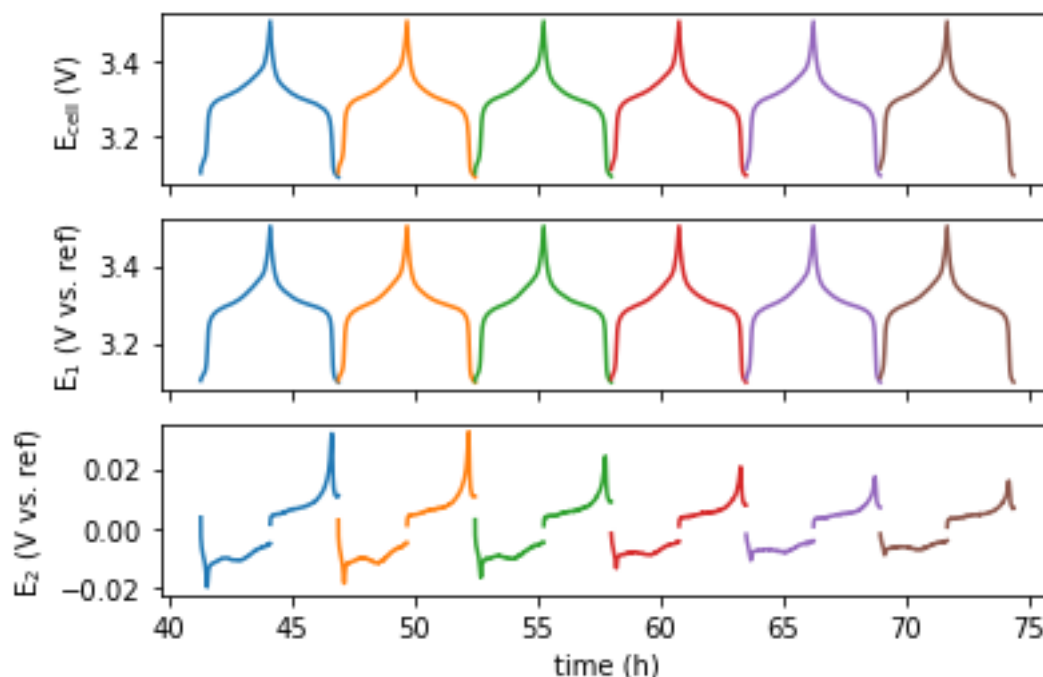| TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	16 / 18

FIGURE 8: A PRUSSIAN WHITE CATHODE CYCLED, ACCORDING TO THE BE NICE PROTOCOL, AGAINST A CARBON COATED ALUMINIUM ANODE, USING A SODIUM REFERENCE ELECTRODE. CYCLE 5 TO 10 ARE SHOWN. E_{CELL} IS THE CELL POTENTIAL, WHAT IS VISIBLE IN TWO-ELECTRODE CYCLING. E_1 AND E_2 ARE THE POTENTIALS OF THE PRUSSIAN WHITE CATHODE AND CARBON COATED ALUMINIUM/SODIUM ANODE RESPECTIVELY. THESE ELECTRODE POTENTIALS ARE SHOWN WITH RESPECT TO A SODIUM REFERENCE ELECTRODE.

The benefit of the *Be nice* protocol is that the potentials within the systems are more predictable. The anode should remain around 0±0.1 V vs. Na+/Na, while the cathode will have a potential between 3.5–3.1 V vs. Na+/Na. This would mean that the side reaction within the cell should be more manageable, e.g. an oxidation of the SEI is less likely. There will be no need to reform any sodium seeds throughout the continued cycling.

The drawback is that any loss in sodium inventory will not be observed at the initial stages. It is first when the reservoir on the anode has been depleted that the inefficiency will properly be observed. This cycling may also be more likely to cause severe dendrite formation.

Protocol 3: "Be mean"

The *be mean* protocol is meant to challenge the sodium plating capabilities of the cell. Here the cell is cycled over a low state of charge, where a sodium reservoir is kept in the cathode. Each cycle, all deposited sodium will be fully removed from the anode. The parameters for this procedure are shown in Table 5 and the resulting cycling curve in Figure 9:

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	17 / 18

TABLE 6 DESCRIPTION OF PROTOCOL 3: "BE MEAN"

Parameters for the *Be mean* cycling procedure.	
Charge	
Capacity restriction (based on Prussian white 150 mA/g)	50 mAh/g
Cell potential cutoff	3.5 V
Current (based on anode nominal area)	1 mA/cm^2
Discharge	
Capacity restriction (based on Prussian white 150 mA/g)	50 mAh/g
Cell potential cutoff	1 V
Current (based on anode nominal area)	-1 mA/cm^2

The benefit of this procedure is that is that loss of sodium inventory will be visible early, by a creeping of the Prussian white's potential profile, rising in potential and eventually traversing to the upper plateau. This also highlights the worst cycling conditions, where there is little control of the potential of the anode, and where a sodium reseeding of the anode will happen about 3 times more often than in the be normal protocol.

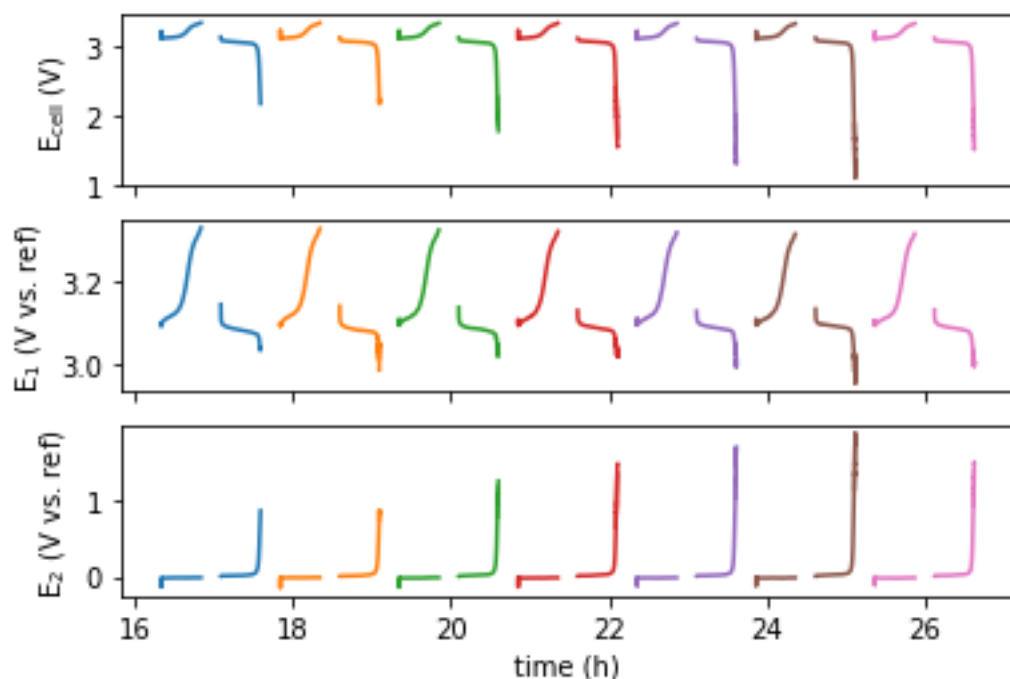The drawbacks of this cycling procedure are thus what is sought to be highlighted.

FIGURE 9: A PRUSSIAN WHITE CATHODE CYCLED, ACCORDING TO THE BE MEAN PROTOCOL, AGAINST A CARBON COATED ALUMINIUM ANODE, USING A SODIUM REFERENCE ELECTRODE. CYCLE 5 TO 10 ARE SHOWN. E$_{CELL}$ IS THE CELL POTENTIAL, WHAT IS VISIBLE IN TWO-ELECTRODE CYCLING. E$_1$ AND E$_2$ ARE THE POTENTIALS OF THE PRUSSIAN WHITE CATHODE AND CARBON COATED ALUMINIUM/SODIUM ANODE RESPECTIVELY. THESE ELECTRODE POTENTIALS ARE SHOWN WITH RESPECT TO A SODIUM REFERENCE ELECTRODE. THIS CYCLING WAS PERFORMED WITH AN ADDITIONAL PAUSE OF 15 MIN BETWEEN CHARGE AND DISCHARGE, THIS IS GENERALLY NOT NECESSARY FOR THE BE MEAN PROTOCOL.

TYPE	Dissemination Level	NAME	REFERENCE			PAGE
			Document ID	Edition/revision	DATE	
R	PU	Report on summary of electrochemical measurements with different electrolytes	D6.1-R-PU-2023	01/00	17/11/2023	18 / 18