SUPPLEMENTAL MATERIAL

Table S1: Parameters of selected LIBs (Molicel INR-21700-P42A) and NIBs (Hakadi 18650-3V)

Parameters	Units	Molicel INR-21700-P42A	Hakadi 18650-3V
Battery Chemistry	-	Lithium	Sodium
Positive electrode	-	Nickel Manganese Cobalt (NMC)	Sodium Metal Oxide
Negative electrode	-	Graphite	Hard Carbon
Electrolyte	-	Lithium Hexafluorophosphate ($LiPF_6$) in organic solvents	Sodium Hexafluorophosphate ($NaPF_6$) in organic solvents
Cell Type	-	Cylindrical	Cylindrical
Size (∅×height)	mm	21.7×70.2	18.4×65.3
Capacity	Ah	4.2	1.53
Nominal Voltage	V	3.6	3.1
Max. Charge current	A	8.4	1.5
Max. Discharge current	A	45	4.5
Charge cut-off	V	4.2	4.1
Discharge cut-off	V	2.5	1.5
Nominal Weight	g	70	87
Rated Charge Temperature Range	° C	-20 ~ 60	-10 ~ 45
Rated Discharge Temperature Range	° C	-40 ~ 60	-30 ~ 60

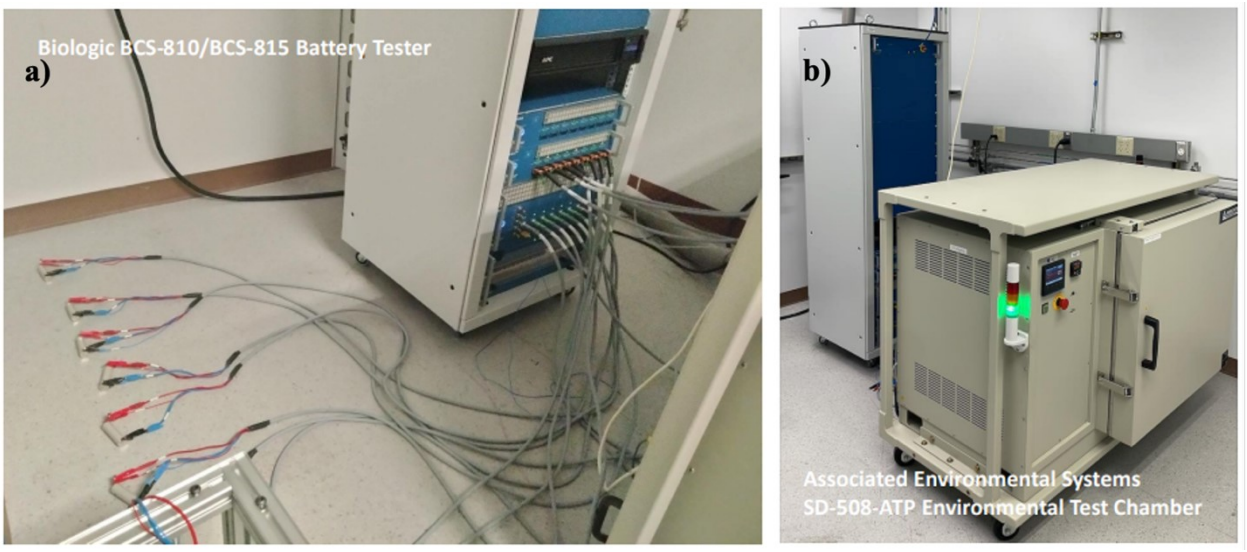

Fig S1. Biologic battery system: **a)** Battery Tester with 24 Channels, **b)** Environmental Chamber that has an Operating range from -40°C ~ 180°C.

Table S2: Test configuration for the first set of experiments

Step	Controls
0	Rest
1	PEIS
2	Rest
3	Constant Current (CC) Charge
4	Constant Voltage (CV) Charge
5	Rest
6	PEIS
7	Rest
8	Constant Current (CC) Discharge
9	Rest
10	Loop to Step 1

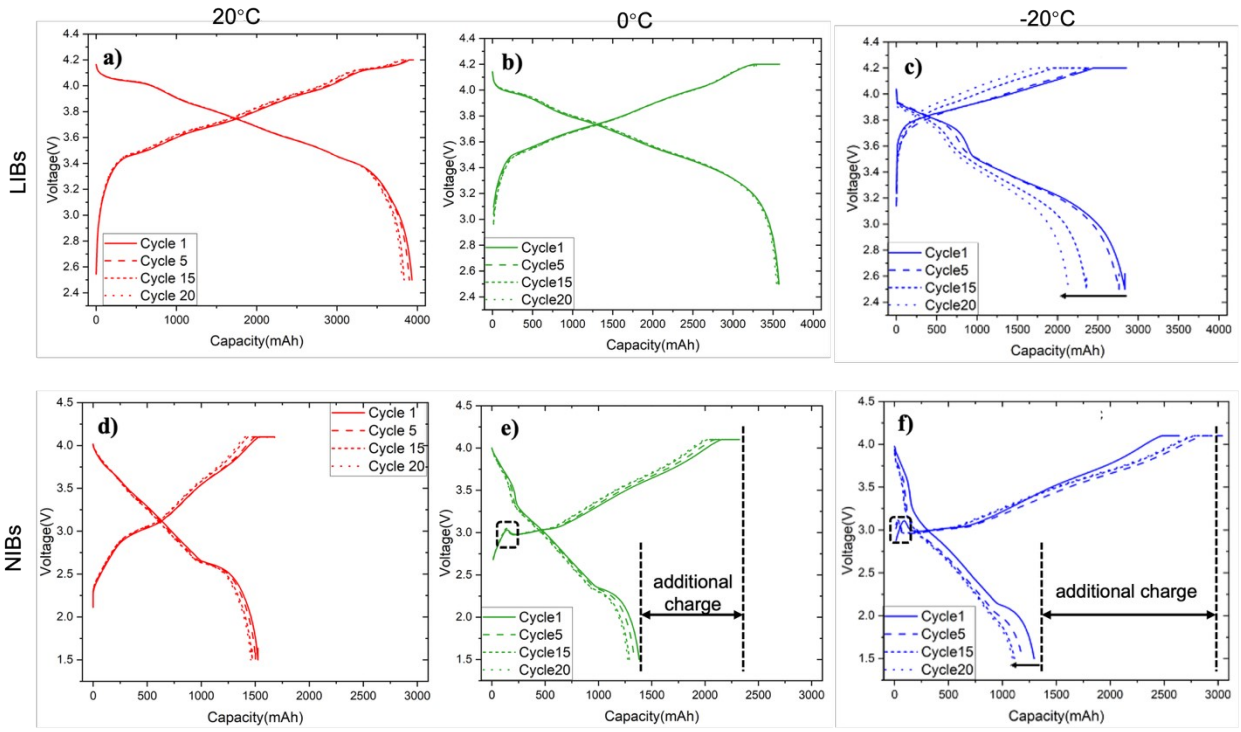

Fig S2. Voltage profiles across different cycles and temperatures: **a)** LIB at 20°C, **b)** LIB at 0°C, **c)** LIB at -20°C, **d)** NIBs at 20°C, **e)** NIB at 0°C, **f)** NIB at -20°C.

Table S3: Electrochemical Impedance Spectroscopy of LIBs and NIBs (Hakadi)

Parameter	Type	-20°C		20°C	
		Discharge(mΩ)	Charge(mΩ)	Discharge(mΩ)	Charge(mΩ)
R_b	LIB	16.3	14.9	12.8	12.5
	NIB	11.6	8.61	18.6	17.8
R_{SEI}	LIB	7.71	20.4	6.02	3.39
	NIB	1180	38.1	13.7	17.8
R_{ct}	LIB	161	48.4	10.6	2.69
	NIB	11100	3810	196	48.5

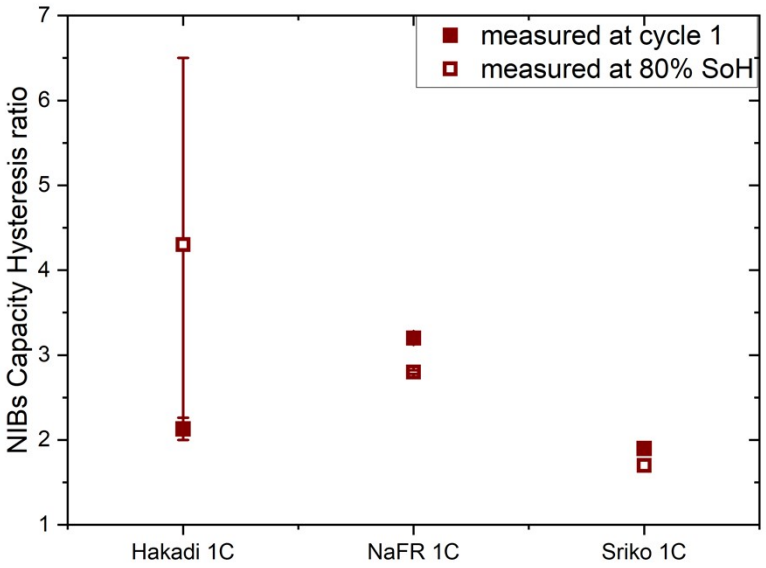

Fig S3. Capacity hysteresis ratios of all the COTS NIBs tested.

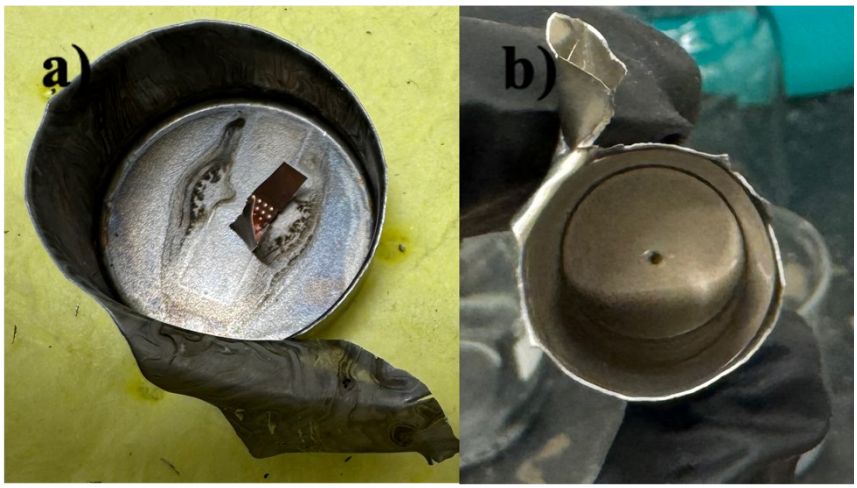

Fig S4. Volume of Electrolyte compared in Fresh cells: **a)** LIBs with no excess electrolyte, **b)** NIBs(Hakadi) with excess quantity.

Fig S5. Demonstration of Sodium Metal on Hard Carbon reacting upon immersion in water.

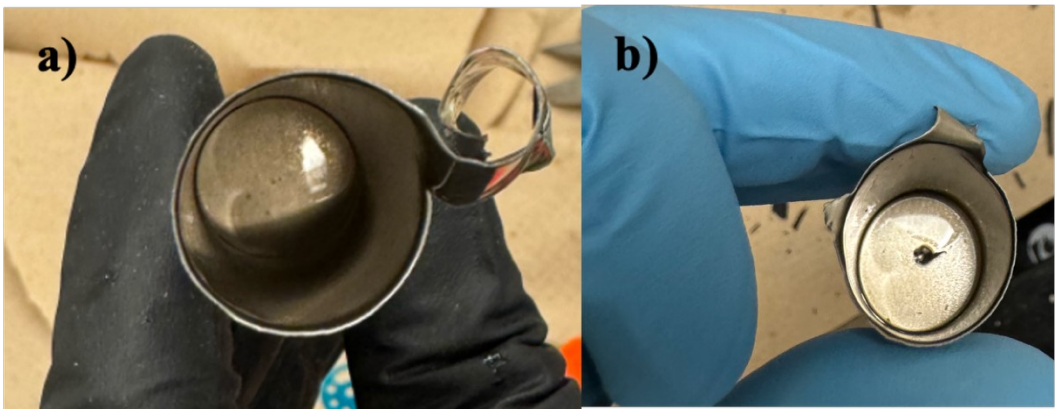

Fig S6. Electrolyte observed inside NIB can after cycling at -20°C: **a)** Excess residue in Hakadi, **b)** No residue in Sriko.

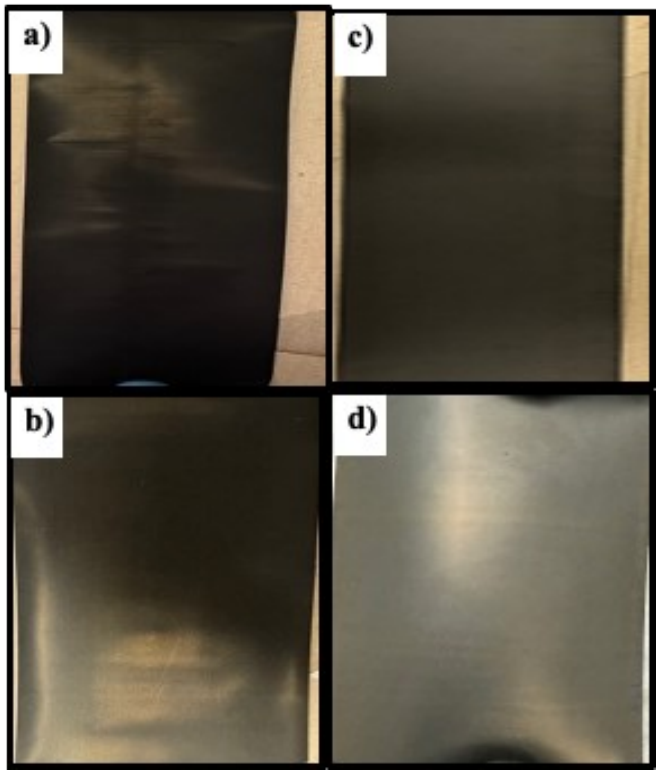

Fig S7. Optical images of positive electrode surfaces before and after cycling at -20°C: **a)** Fresh Hakadi, **b)** -20°C Hakadi, **c)** Fresh Sriko, **d)** -20°C Sriko.

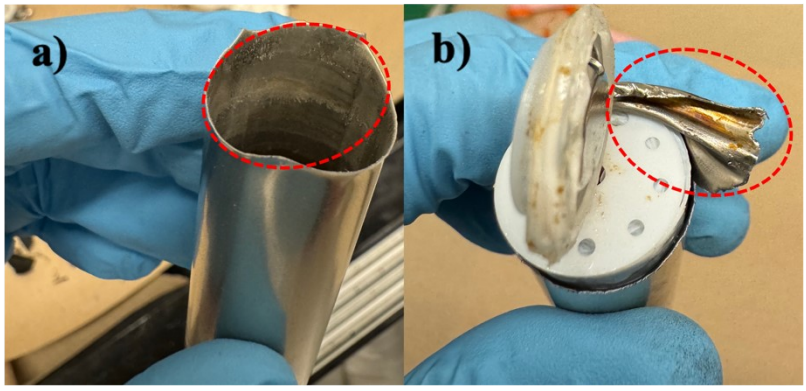

Fig S8. Corrosion of battery can after cycling at -20°C: **a)** Hakadi, **b)** Sriko.

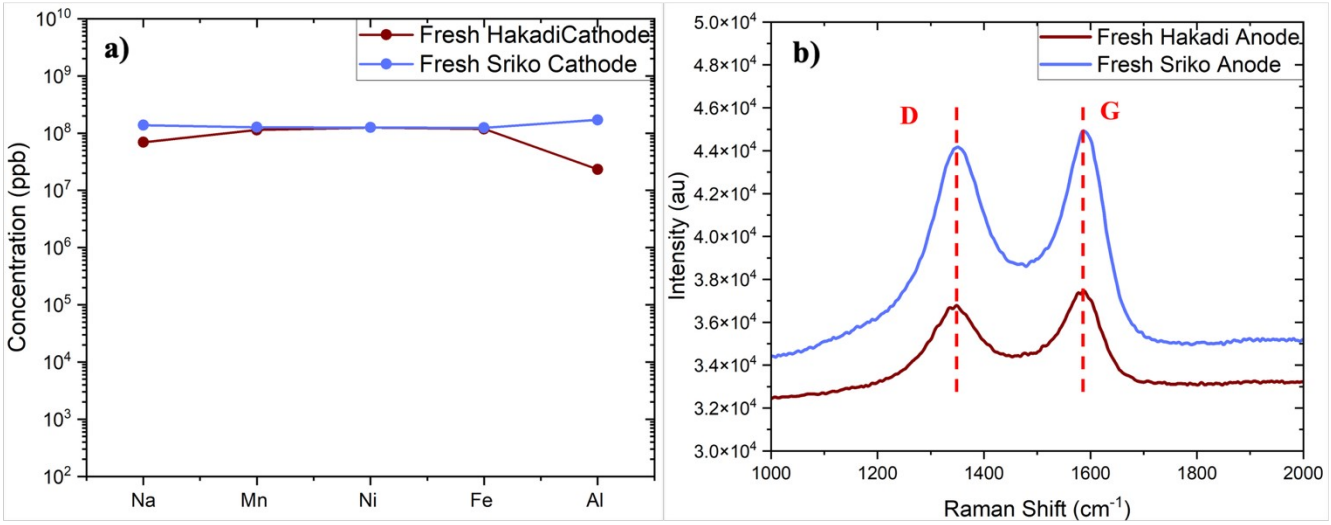

Fig S9. Material characterization of fresh electrodes from Hakadi and Sriko cells: **a)** ICP-MS analysis confirming the positive electrode composition as NMF 111, **b)** Raman Spectroscopy confirming the negative electrode material as Hard Carbon.

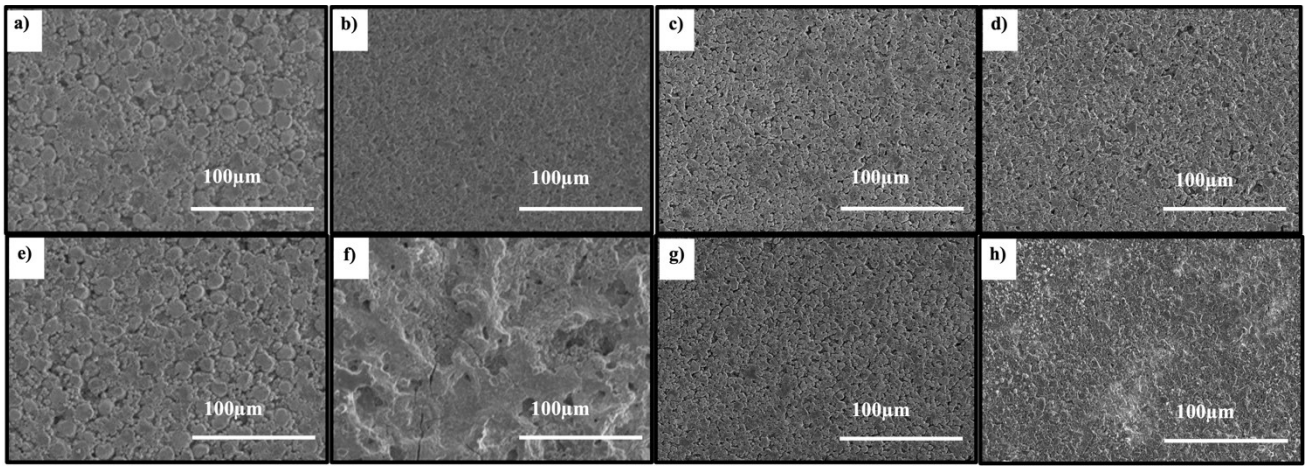

Fig S10. SEM images of electrodes before (100% SoH) and after (80% SoH) cycling at -20°C: **a)** Fresh Hakadi positive electrode, **b)** Fresh Hakadi negative electrode, **c)** Fresh Sriko positive electrode, **d)** Fresh Sriko negative electrode, **e)** -20°C Hakadi positive electrode, **f)** -20°C Hakadi negative electrode, **g)** -20°C Sriko positive electrode, **h)** -20°C Sriko negative electrode. Significant surface changes, cracking and salt depositions are observed in **f) & h)** compared to their corresponding fresh negative electrodes.

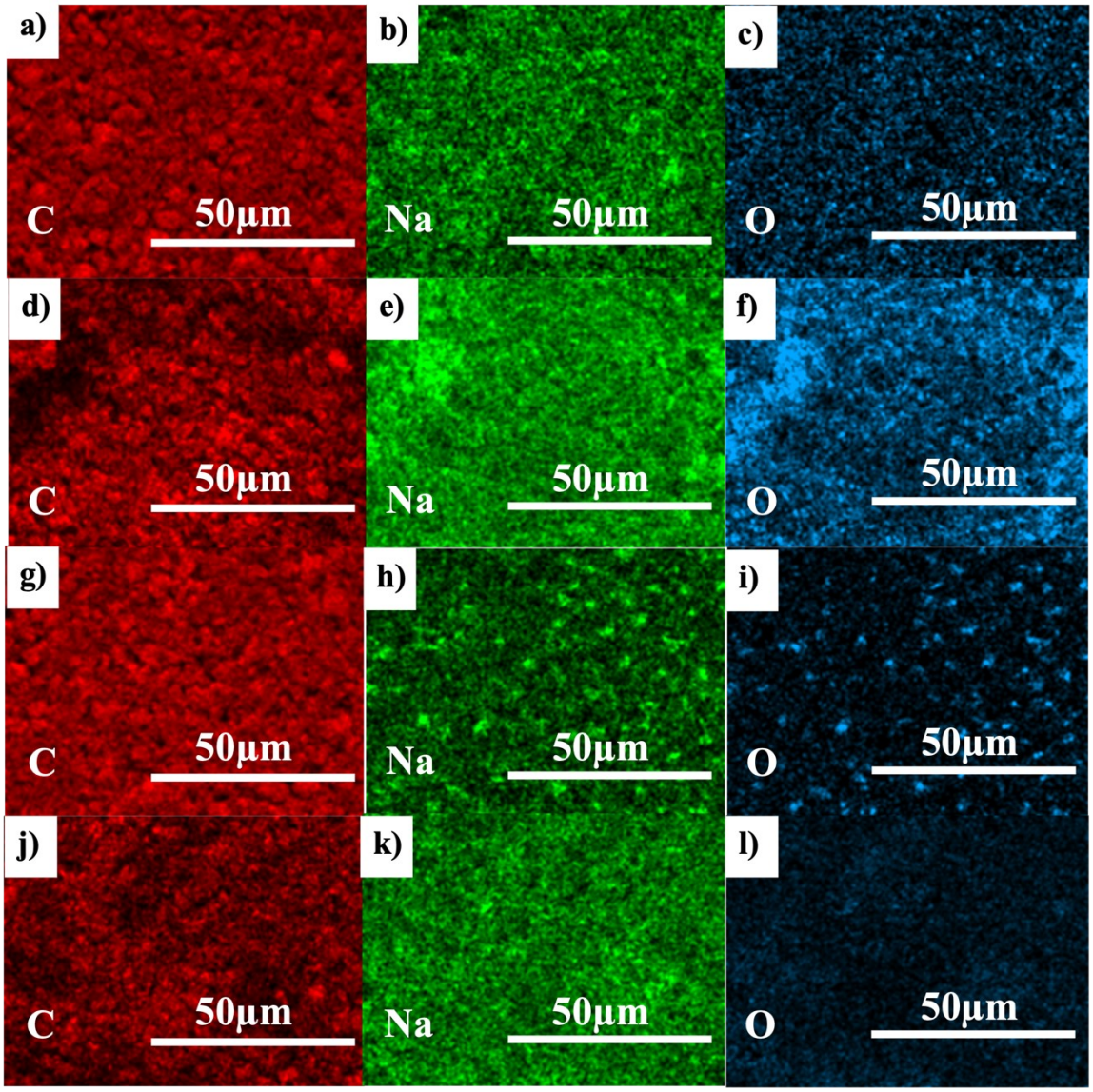

Fig S11. EDS images of hard carbon electrodes before (100% SoH) and after (80% SoH) cycling at -20°C: **a)**, **b)** & **c)** Fresh Hakadi, **d)**, **e)** & **f)** -20°C Hakadi, **g)**, **h)** & **i)** Fresh Sriko, **j)**, **k)** & **l)** -20°C Sriko. Significant sodium deposition on hard carbon after cycling compared to their corresponding fresh electrodes.

Fig S12. Sodium metal deposition observed on hard carbon negative electrode of Hakadi after testing for 5 cycles at -20°C.

Table S4a: GC-MS analysis of fresh Hakadi electrolyte

	Retention Time (RT)	Compound Name	Area %
Hakadi	1.303	Phosphoryl Fluoride	0.17
	3.348	Ethyl methyl Carbonate	31.44
	9.831	1,3-Dioxolan-2-one,4-methyl	23.42
	10.103	Propylene Carbonate	16.54
	9.416	Thiolane-3,4-dicarbonitrile, 2,5-di-tert-butyl-3,4-bis(trifluoromethyl)	14.71
	2.105	Dimethyl Ester Carbonate	8.82
	12.603	1,2-Oxathiolane,2,2-dioxide	1.23

Table S4b: GC-MS analysis of fresh Sriko electrolyte

	Retention Time (RT)	Compound Name	Area %
Sriko	1.303	Phosphoryl Fluoride	0.23
	9.707	Propylene Carbonate	54.67
	3.363	Ethyl methyl Carbonate	27.97
	4.754	Diethyl Carbonate	7.61
	9.83	Thiolane-3,4-dicarbonitrile, 2,5-di-tert-butyl-3,4-bis(trifluoromethyl)	7.07
	2.067	Dimethyl Carbonate	1.00