Supporting Information

A lignosulfonate binder for hard carbon anodes in sodium-ion batteries: a comparative study

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1. Charge balance calculation for full cell fabrication:

Charge balance calculation for full cell fabrication is very well known in battery chemistry.[1] For balancing the full cell, hard carbon (HC) and Prussian white (PW), half-cell performances were used to determine their specific capacities (Q) and Coulombic efficiencies (CE):

Anode: Q_{HC} = 270 mAh g^{-1}, CE_{HC} = 99%, Active material loading = 95%

Cathode: Q_{PW} = 155 mAh g^{-1}, CE_{PW} = 99% Active material loading = 85%

In full cell,

$$Anode\ Areal\ Capacity = Cathode\ Areal\ Capacity \quad \text{Eq. S1}$$

Or,

$$QHC * \frac{HC\ active\ mass\ loading}{CEHC} = QPW * \frac{PW\ active\ mass\ loading * n}{CEPW} \quad \text{Eq. S2}$$

Here, n is the number to determine to make a charge balanced full cell, keeping our anode mass loading a known value. HC and PW denote the overall mass of anode and cathode, respectively.

$$270 * \frac{HC * 0.95}{0.99} = 155 * \frac{PW * 0.85}{0.99} * n \quad \text{Eq. S3}$$

$$259.09 * HC = 133.08 * PW * n \quad \text{Eq. S4}$$

$$HC = 1.9 * PW \quad \text{Eq. S5}$$

Thus, PW for full cells was taken as 1.9 times of HC.

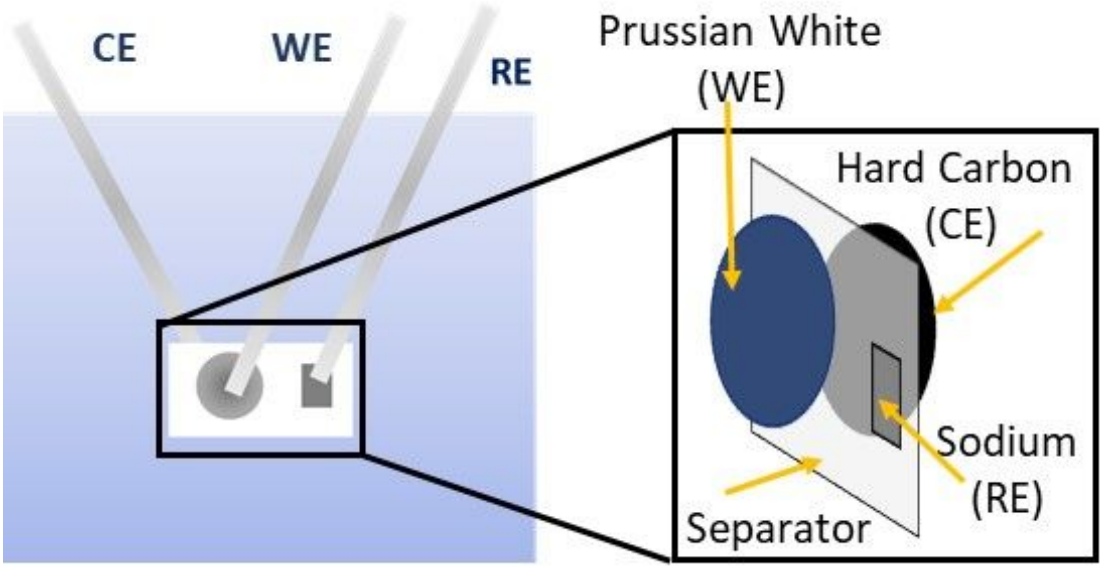

Figure S1. Schematic representation of full cell in 3 electrode configuration (left) with zoom in of working, counter and refernece electrode (WE, CE and RE) along with separator (right).

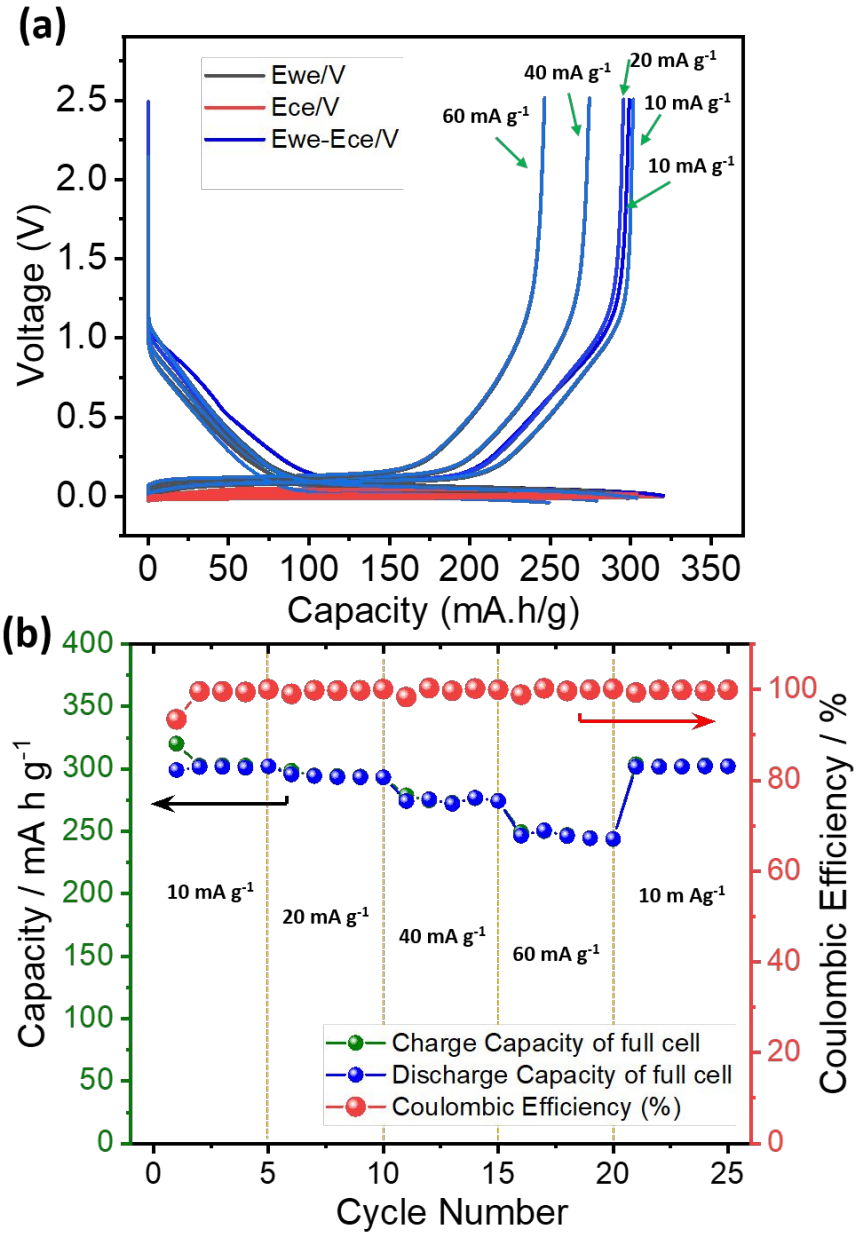

Figure S2. Determination of the maximum capacity of hard carbon. (a) Voltage profile of hard carbon using CMC binder in three electrodes half cell configuration at different current rates (10, 20, 40, 60 and 10 mA g^{-1}) in $NaPF_6$/EC:DEC electrolyte. (b) Corresponding cycling performance and Coulombic efficiency of CMC based hard carbon electrode in $NaPF_6$/EC:DEC electrolyte at different current rates.

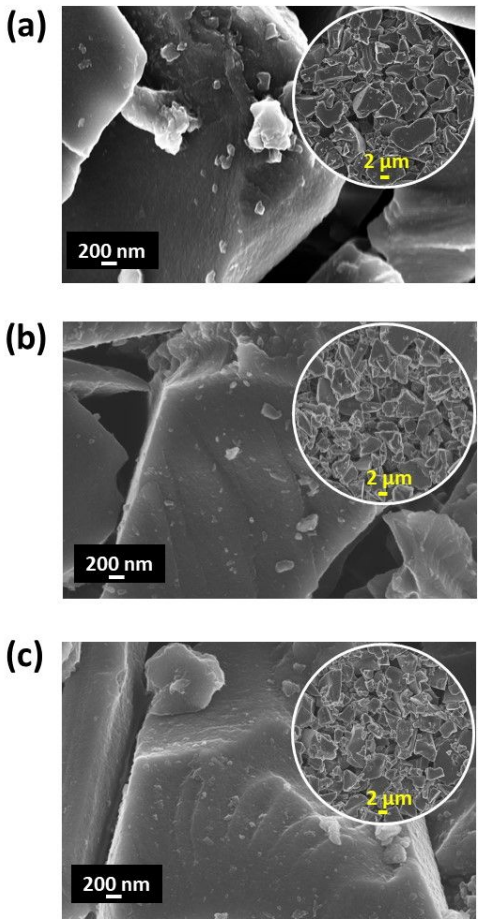

Figure S3. The SEM images of hard carbon electrodes composed of (a) Lg binder, (b) CMC binder and (c) Alg binder.

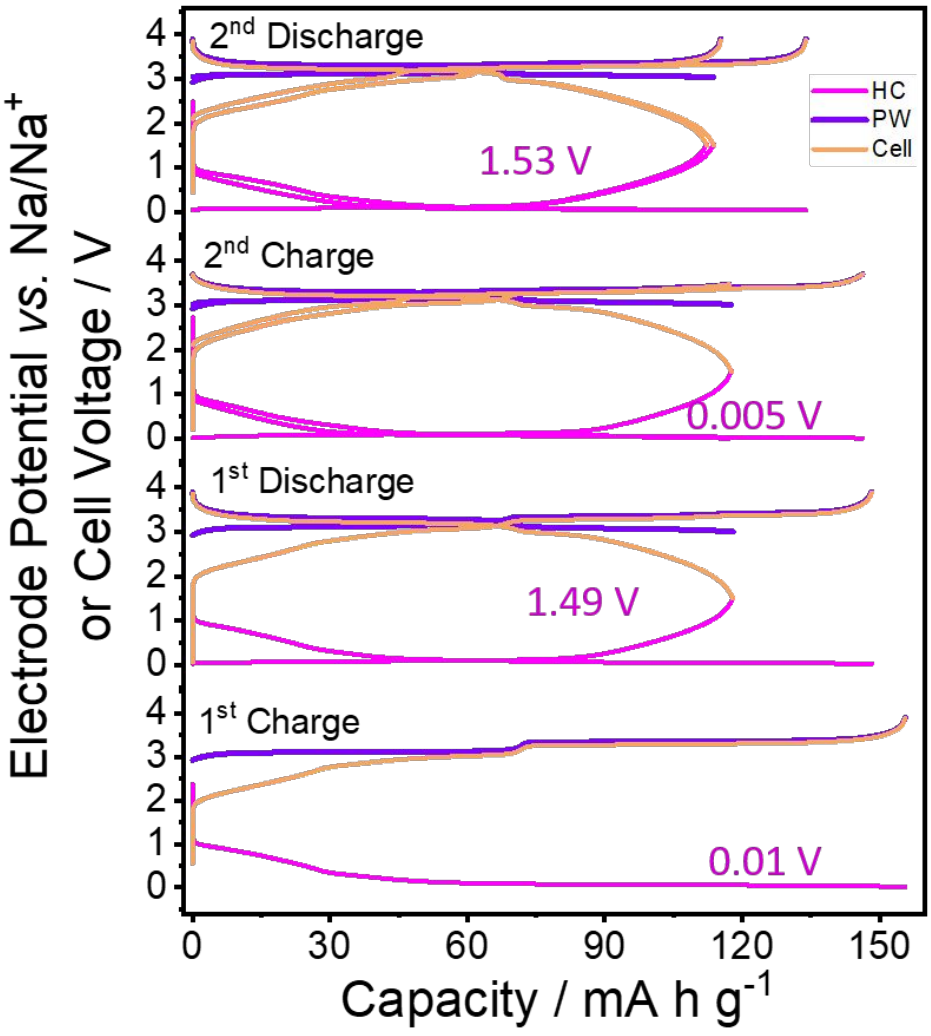

Figure S4. LgSA based hard carbon electrodes cycled in full cell (in 3 electrode configuration) at different potentials in $NaPF_6$/EC:DEC electrolyte.

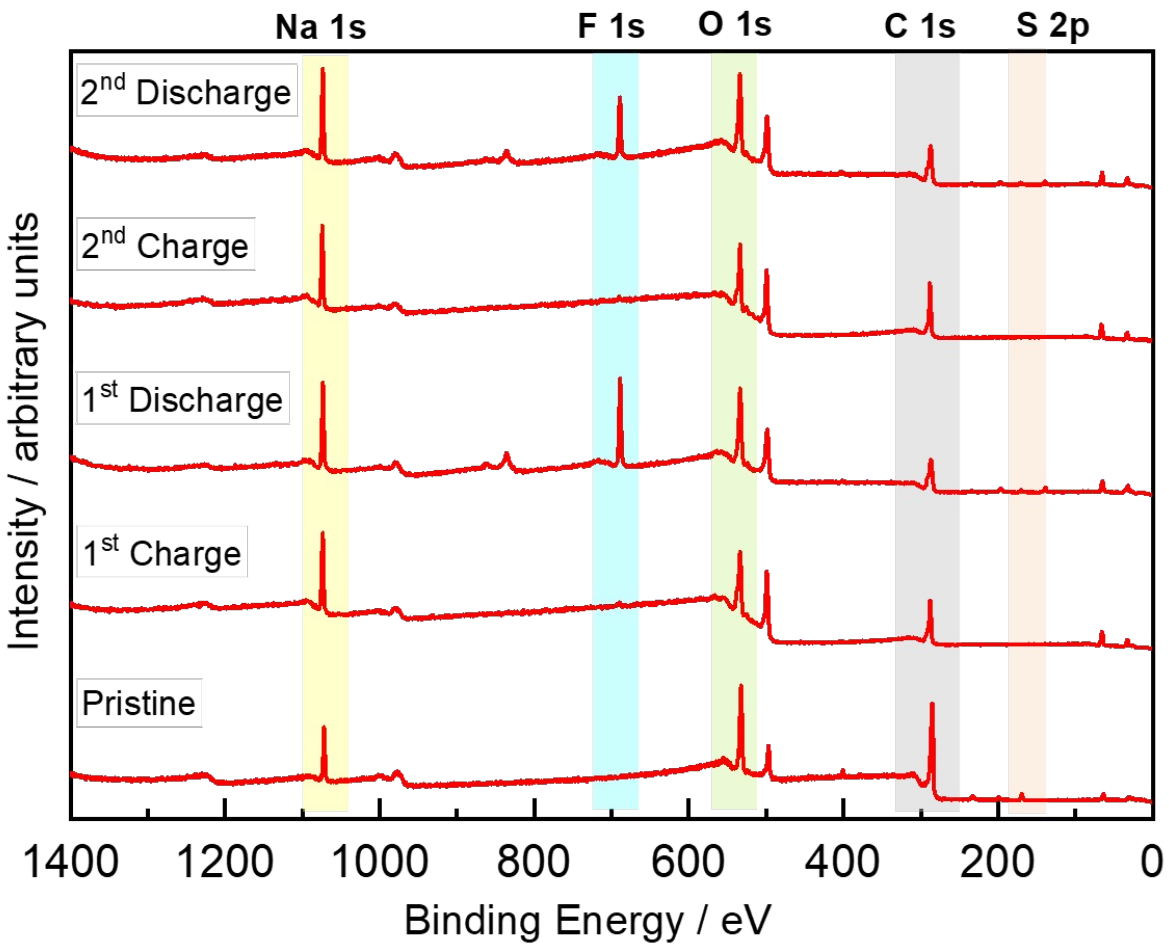

Figure S5. XPS survey spectra showing the presence of Na 1s, F 1s (absent in pristine), O 1s, C 1s and S 2p peaks for pristine and cycled LgSA based hard carbon electrodes in full cell, where discharge and charge represents the state of charge of hard carbon.

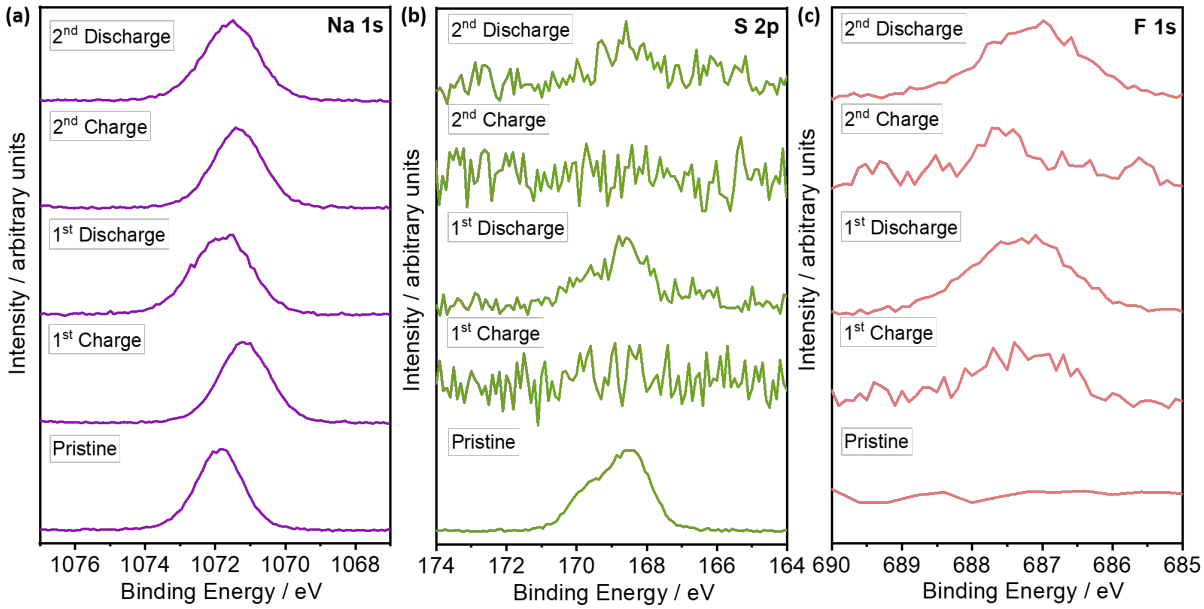

Figure S6. (a) Na 1s, (b) S 2p and (c) F 1s XPS spectra for pristine LgSA and cycled LgSA based hard carbon electrode in $NaPF_6$/EC:DEC electrolyte in full cell configuration. Spectra are normalized except F 1s spectrum for the pristine sample due to absence of F element as expected.

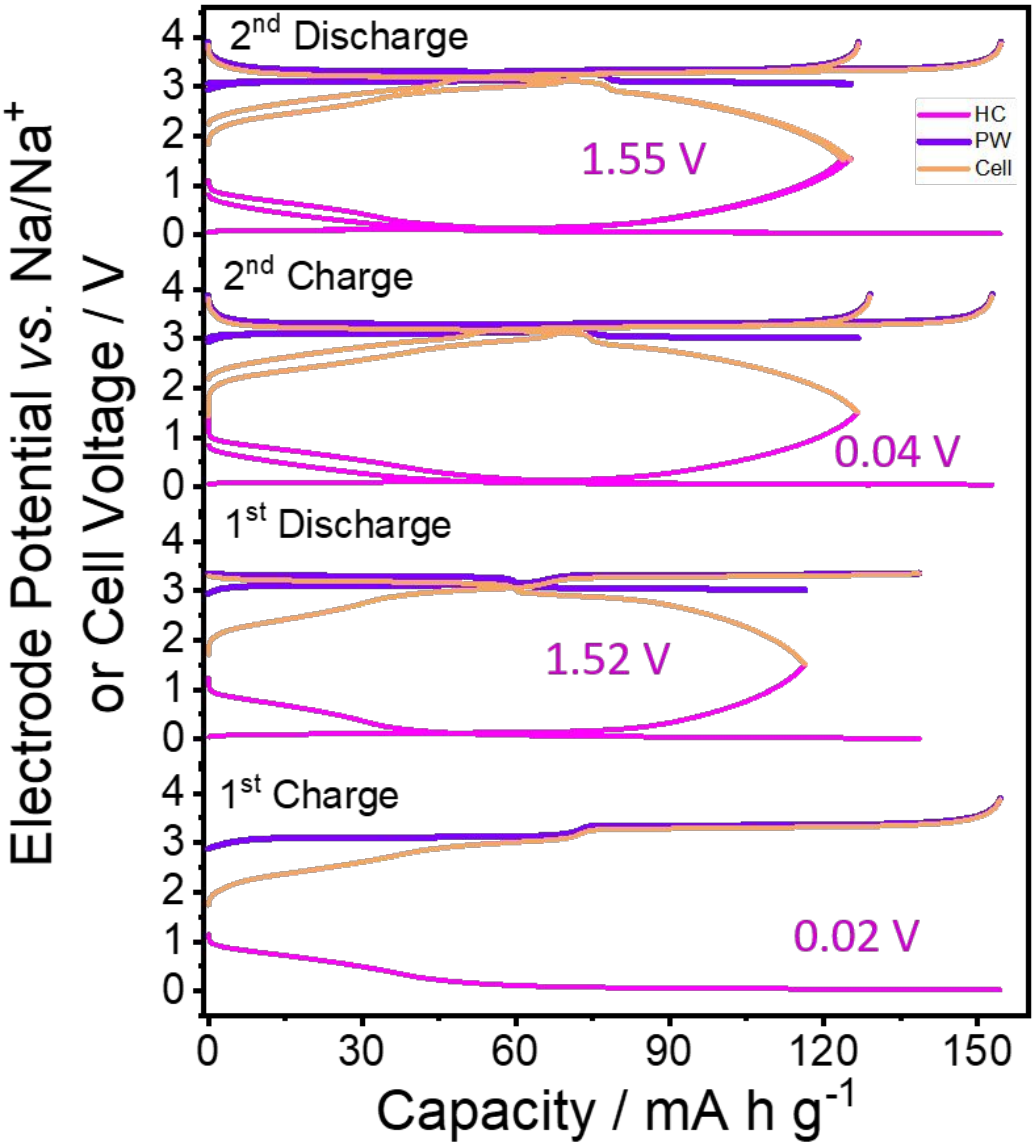

Figure S7. CMC based hard carbon electrodes cycled in full cell (in 3 electrode configuration) at different potentials in $NaPF_6$/EC:DEC electrolyte.

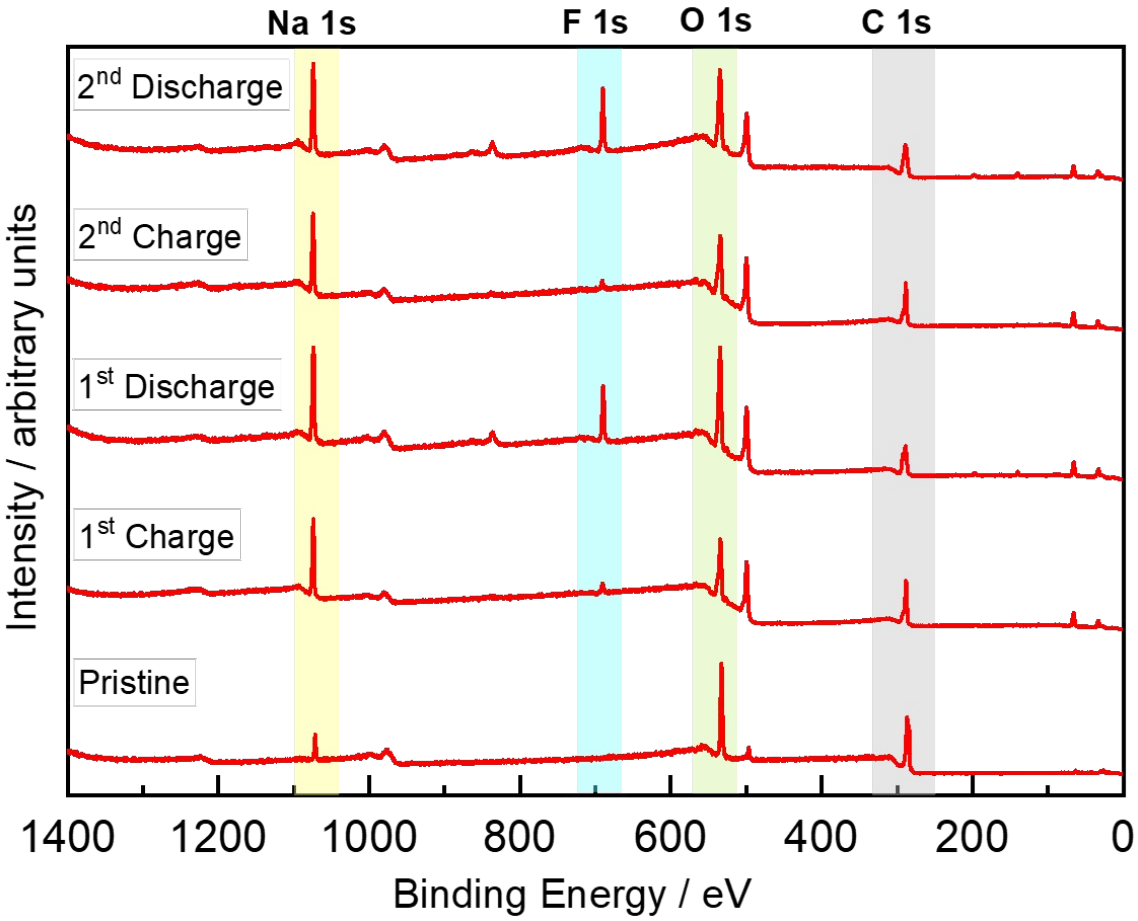

Figure S8. XPS survey spectra showing the presence of Na 1s, F 1s (absent in pristine), O 1s and C 1s peaks for pristine and cycled CMC based hard carbon electrodes in full cell, where discharge and charge stands for hard carbon state of charge.

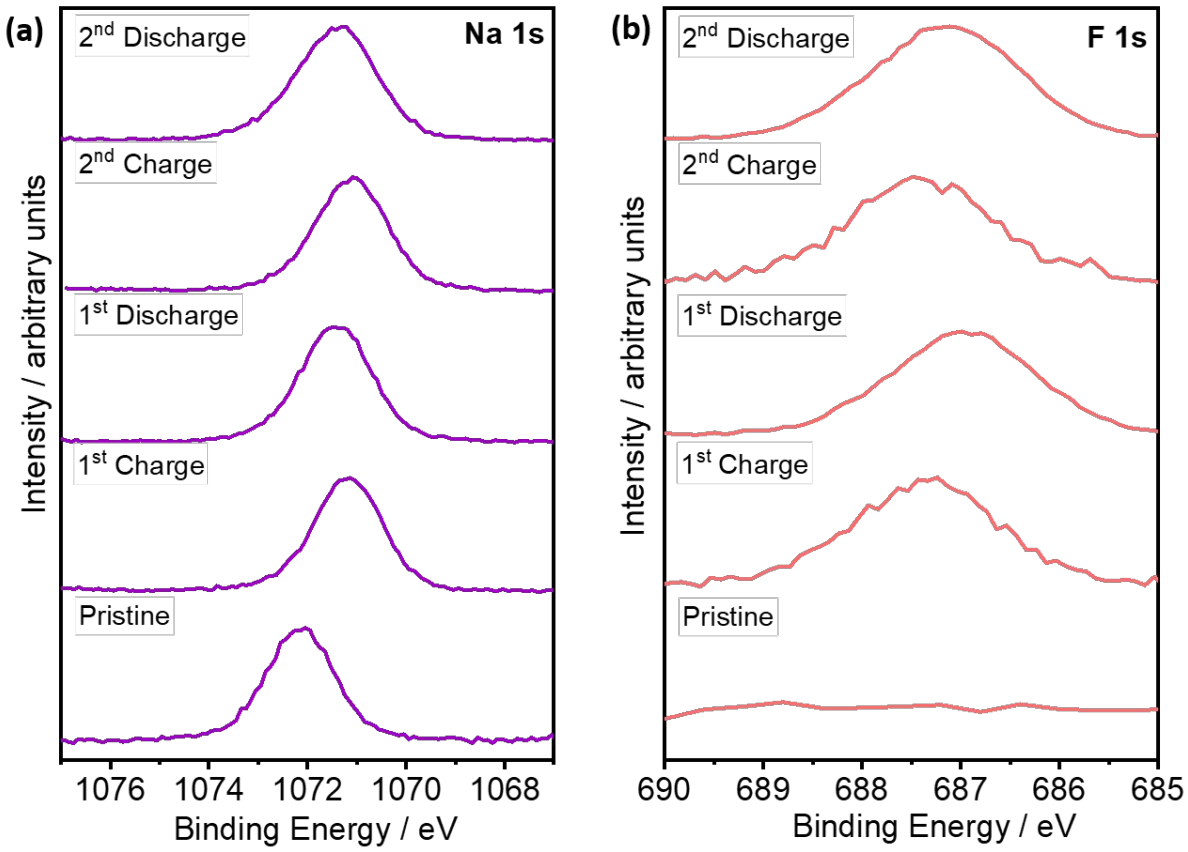

Figure S9. (a) Na 1s and (b) F 1s XPS spectra for pristine CMC and cycled CMC based hard carbon electrode in $NaPF_6$/EC:DEC electrolyte in full cell configuration. Spectra are normalized except F 1s spectrum for the pristine sample due to absence of F peak as expected.

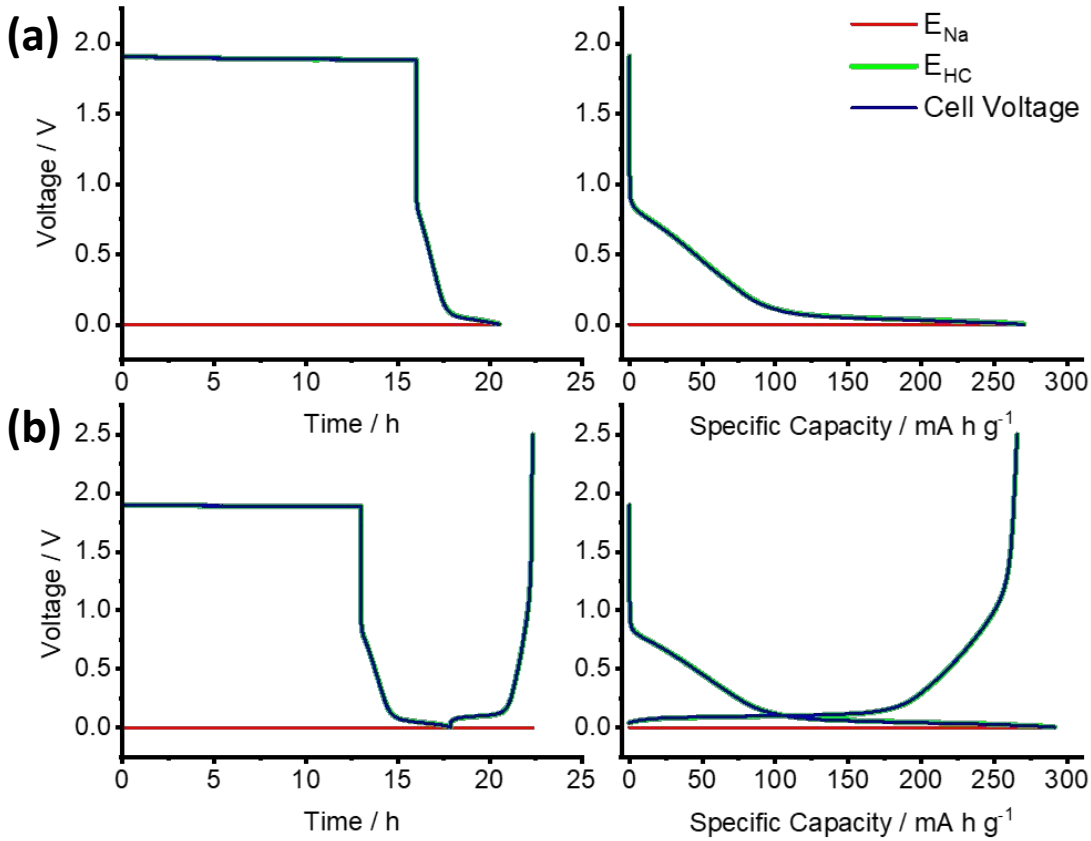

Figure S10. (a) LgSA based hard carbon electrodes with stable OCV, cycled in half-cell condition (3 electrode configuration) to 0.005 V as 1st discharge, and (b) 1st charge to 2.5 V.

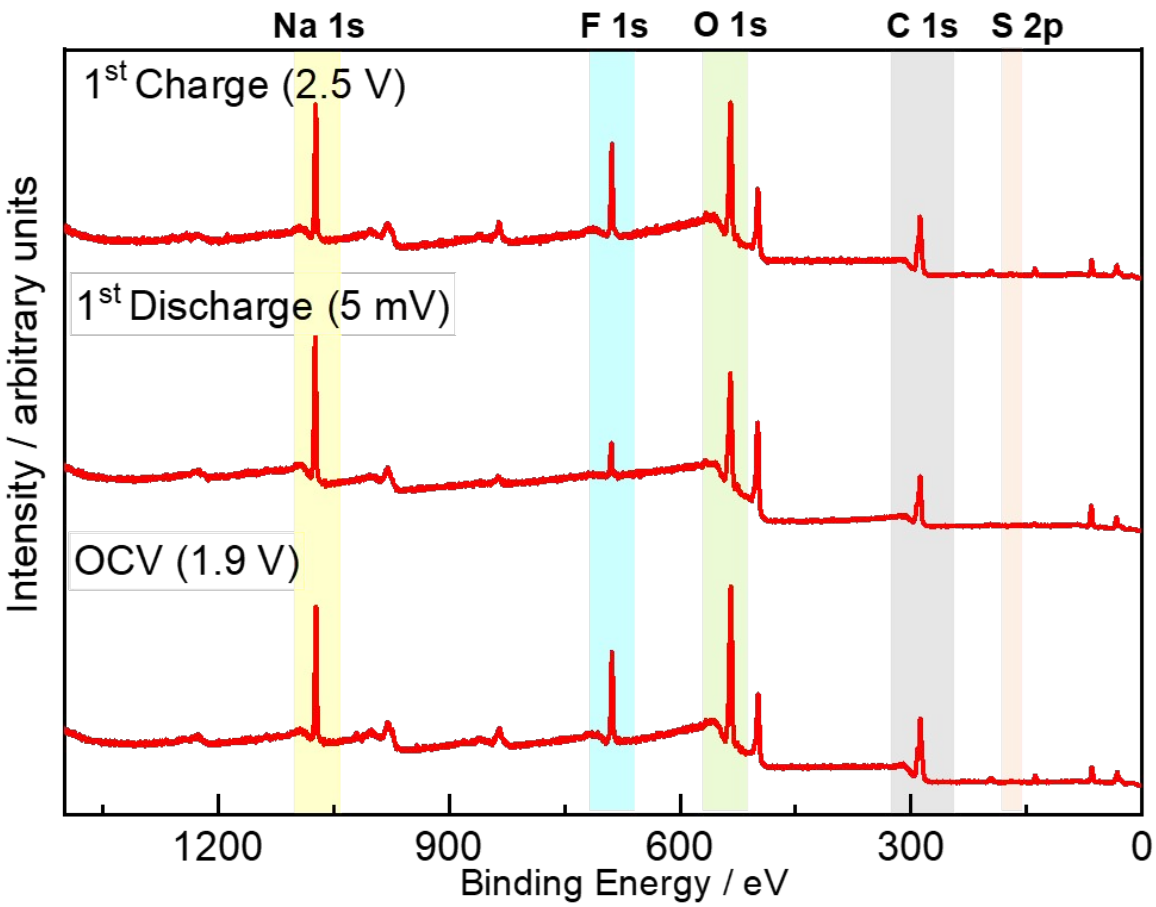

Figure S11. XPS survey spectra showing the presence of Na 1s, F 1s, O 1s, C 1s and S 2p peaks in cycled LgSA based hard carbon electrodes.

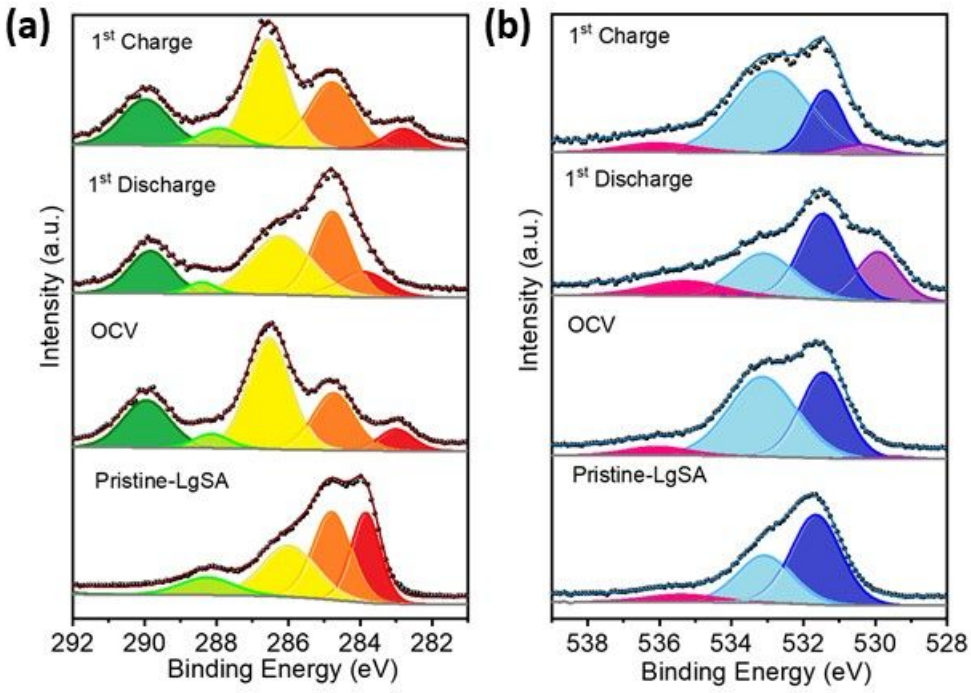

Figure S12. Normalized XPS spectra of (a) C 1s and (b) O 1s in pristine and cycled LgSA based hard carbon electrode in half cell using $NaPF_6$/EC:DEC electrolyte. Peak assignments; C 1s: sp^2 C=C/Na_xC (red), sp^3 C (orange), C-O (yellow), C=O (light green), O-C=O/CO_3^{2-} (dark green), C-Cl (pink); O 1s: Na_2O (purple), C=O/CO_3^{2-} (dark blue), C-O (light blue), Na KLL Auger (magenta).

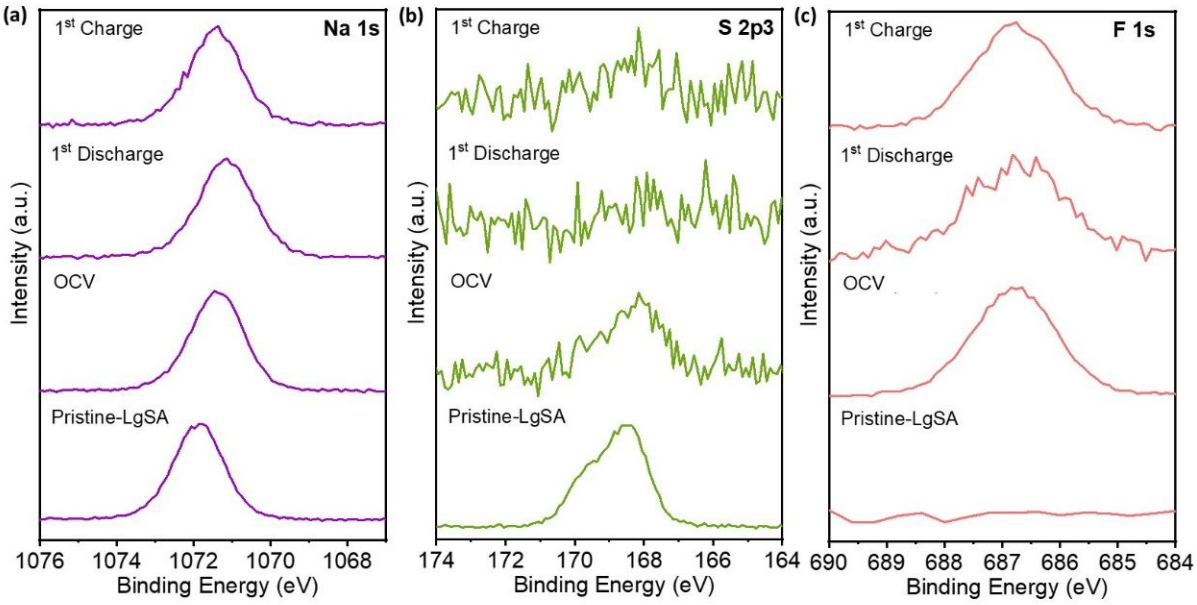

Figure S13. (a) Na 1s, (b) S 2p and (c) F 1s XPS spectra for pristine, soaked (OCV) and cycled LgSA based hard carbon electrode in $NaPF_6$/EC:DEC electrolyte in half-cell configuration. Spectra are normalized except F 1s spectrum for the pristine sample represented as pristine-LgSA due to non-appearance of F peak as expected.

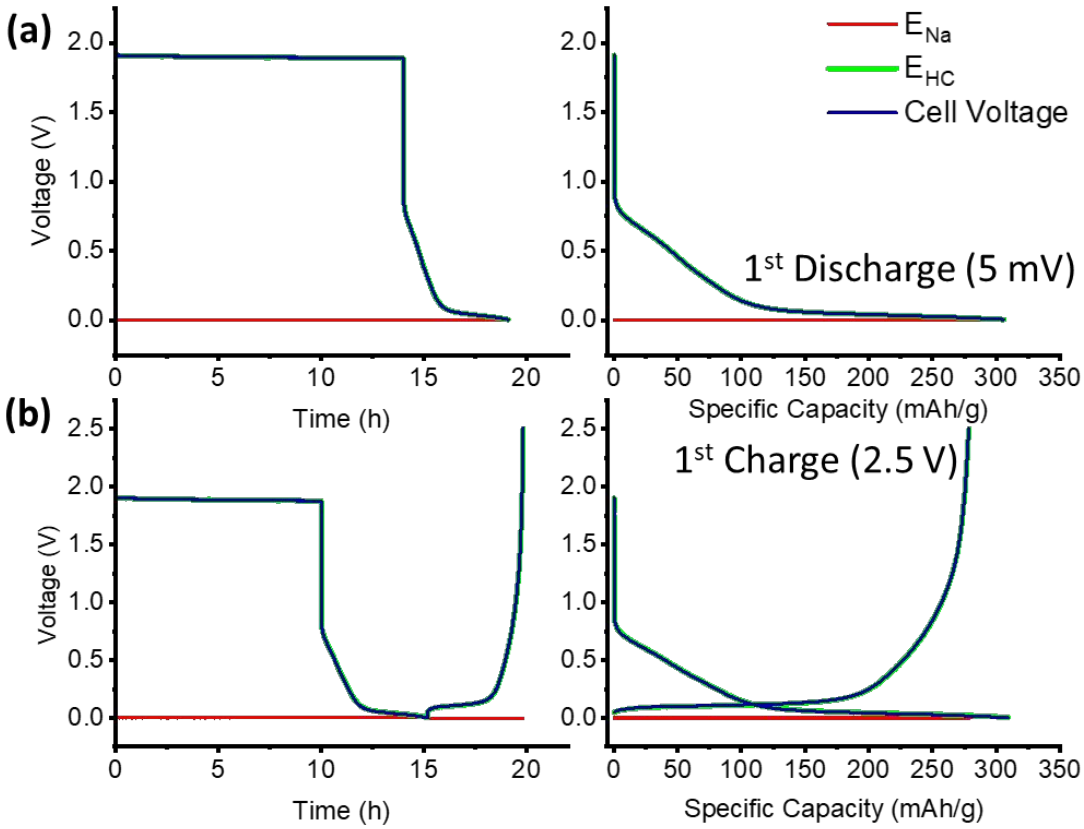

Figure S14. (a) CMC based hard carbon electrodes with stable OCV, cycled in half-cell condition to 0.005 V as 1st discharge, and (b) 1st charge to 2.5 V.

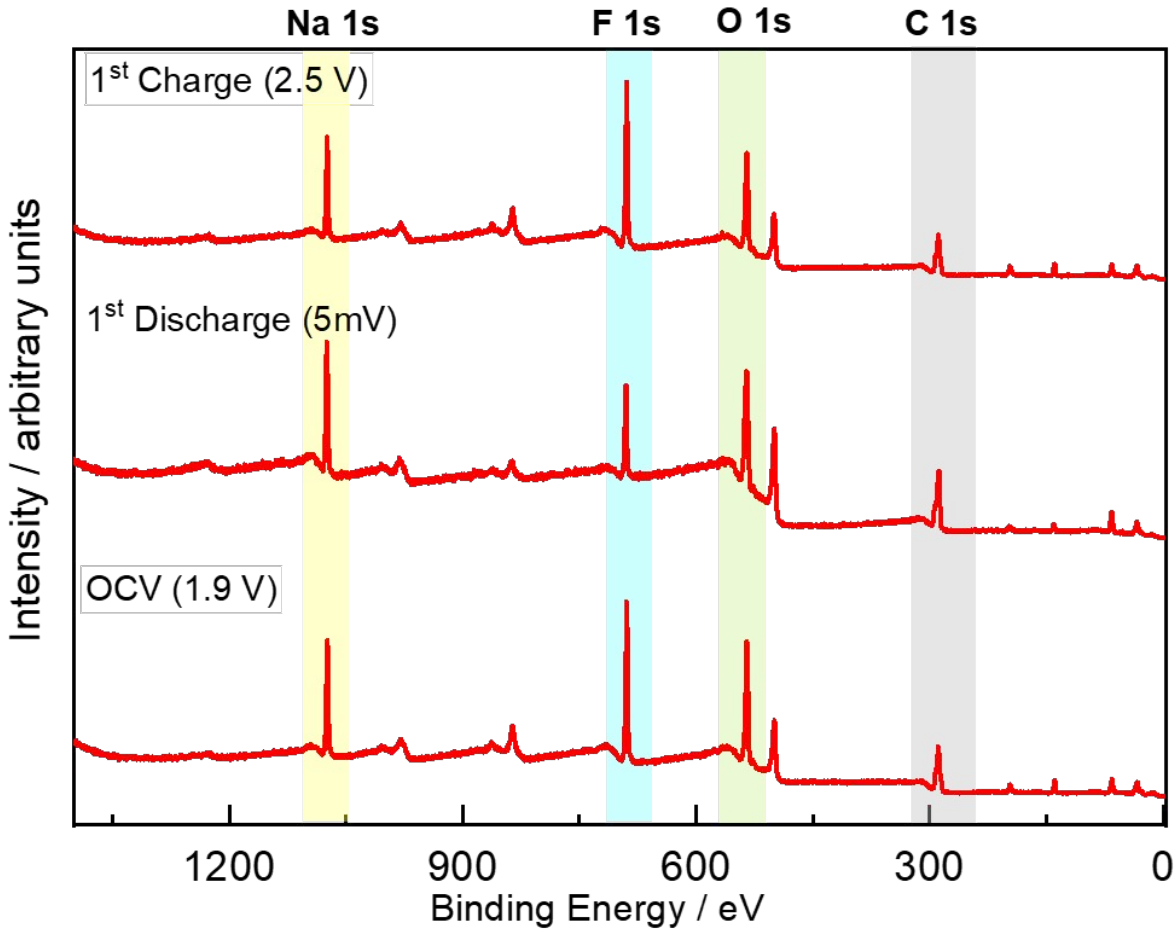

Figure S15. XPS survey spectra showing the presence of Na 1s, F 1s, O 1s and C 1s peaks in cycled CMC based hard carbon electrodes.

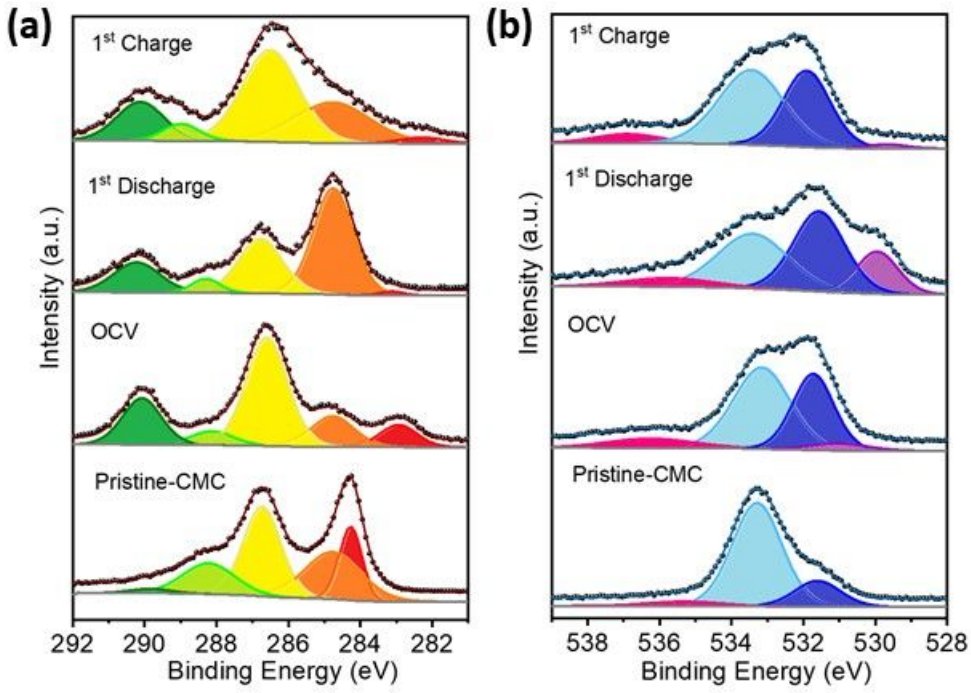

Figure S16. Normalized XPS spectra of (a) C 1s and (b) O 1s in pristine and cycled CMC based hard carbon electrode in half-cell configuration in $NaPF_6$/EC:DEC electrolyte. Peak assignments; C 1s: sp^2 C=C/Na_xC (red), sp^3 C (orange), C-O (yellow), C=O (light green), O-C=O/CO_3^{2-} (dark green), C-Cl (pink); O 1s: Na_2O (purple), C=O/CO_3^{2-} (dark blue), C-O (light blue), Na KLL Auger (magenta).

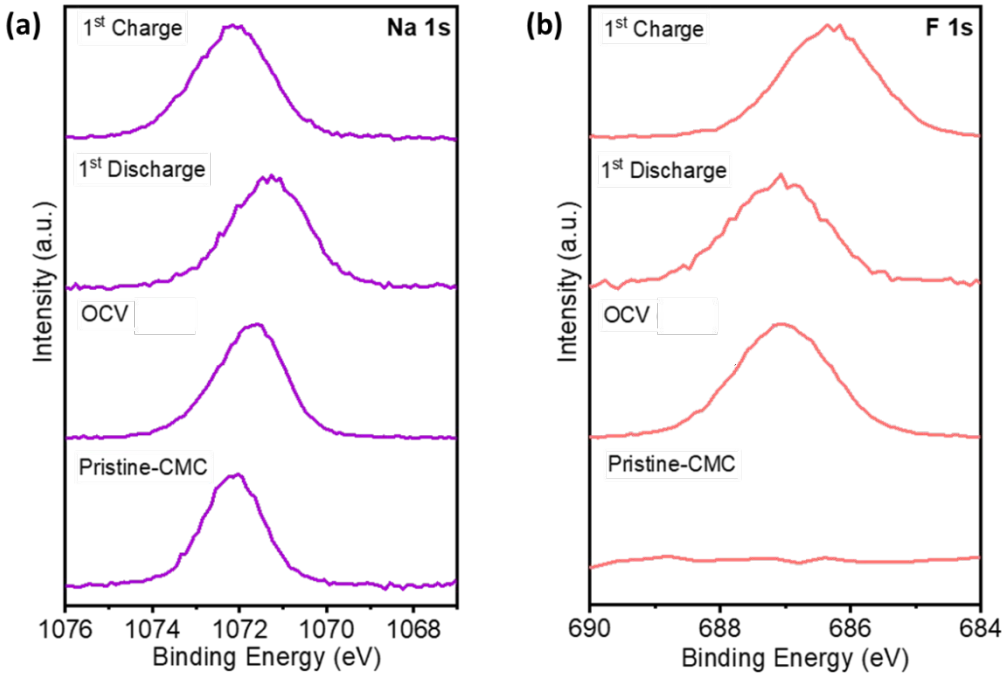

Figure S17. (a) Na 1s and (b) F 1s XPS spectra for pristine, soaked (OCV) and cycled CMC based hard carbon electrode in $NaPF_6$/EC:DEC electrolyte in half-cell configuration. Spectra are normalized except F 1s spectrum for the pristine sample represented as pristine-CMC due to non-appearance of F peak as expected.

Table S1. Binding energies for peaks fitted in C 1s XPS spectra for LgSA and CMC based pristine and cycled hard carbon electrodes in full cell.

HC Anode (in full cell)	C=C/Na_xC	C-C	C-O	C=O	O-C=O/CO_3^{2-}
	Binding energy (eV)				
LgSA					
Pristine	283.8488	284.7949	285.9880	288.2522	
1st Charge	283.4070	284.8313	285.9746	288.4331	290.3055
1st Discharge	283.1218	284.8280	286.5784	288.5990	290.0048
2nd Charge	283.4423	284.7708	285.3256	288.4127	290.2187
2nd Discharge	283.0400	284.7571	286.4335	288.4026	289.8098
CMC					
Pristine	284.2656	284.7661	286.7300	288.2181	289.8412
1st Charge	283.3634	284.7722	285.4800	288.4142	289.8628
1st Discharge	283.1335	284.7507	286.4942	288.4251	289.8360
2nd Charge	283.2235	284.7873	286.2519	288.3778	290.0709
2nd Discharge	282.9589	284.7654	286.4389	288.3748	289.8485

Table S2. Binding energies for peaks fitted in O 1s XPS spectra for LgSA and CMC based pristine and cycled hard carbon electrodes in full cell.

HC Anode (in full cell)	Na_2O	C=O/ CO_3^{2-}	C-O	Na KLL
	Binding energy (eV)			
LgSA				
Pristine		531.6470	533.0762	535.3840
1st Charge	530.1209	531.3612	533.0319	534.8842
1st Discharge	530.9958	531.7109	533.3200	535.9740
2nd Charge	530.3633	531.4815	532.0768	535.1350
2nd Discharge	530.1516	531.3910	532.9135	535.8065
CMC				
Pristine		531.6030	533.2853	535.3234
1st Charge	530.0078	531.2822	533.2508	535.1939
1st Discharge	529.8834	531.5310	533.2245	535.5650
2nd Charge	530.0595	531.3216	533.2215	535.1447
2nd Discharge	529.5303	531.2421	532.9704	535.3657

Table S3. Binding energies for peaks fitted in C 1s XPS spectra for LgSA and CMC based pristine, soaked (OCV), cycled hard carbon electrodes in half-cell.

HC Anode (in half-cell)	C=C/ Na_xC	C-C	C-O	C=O	O-C=O/CO_3^{2-}
	Binding energy (eV)				
LgSA					
Pristine LgSA	283.8488	284.7949	285.9880	288.2522	
OCV	283.0036	284.7450	286.5354	288.1432	289.9478
1st Discharge	283.8987	284.7832	286.2114	288.4033	289.8370
1st Charge	282.7994	284.7895	286.5720	287.9350	289.9763
CMC					
Pristine LgSA	284.2656	284.7661	286.7300	288.2181	289.8412
OCV	282.9355	284.7687	286.6016	288.1269	290.0747
1st Discharge	283.1205	284.7529	286.7779	288.2927	290.2195
1st Charge	282.2722	284.7737	286.5064	288.9830	290.1194

Table S4. Binding energies for peaks fitted in O 1s XPS spectra for LgSA and CMC based pristine, soaked (OCV), cycled hard carbon electrodes in half-cell.

HC Anode (in half-cell)	Na_2O	C=O/ CO_3^{2-}	C-O	Na KLL
	Binding energy (eV)			
LgSA				
Pristine LgSA		531.6470	533.0762	535.3840
OCV	529.6078	531.4482	533.1318	536.0653
1st Discharge	529.9195	531.4534	533.0949	535.2977
1st Charge	530.4131	531.3816	532.9043	536.0544
CMC				
Pristine CMC		531.6030	533.2853	535.3234
OCV	531.0285	531.7239	533.1550	536.2441
1st Discharge	529.9418	531.5600	533.4058	535.7462
1st Charge	529.6815	531.9061	533.4433	536.8851

References

(S1) Kasnatscheew, J.; Placke, T.; Streipert, B.; Rothermel, S.; Wagner, R.; Meister, P.; Laskovic, I. C.; Winter, M. A Tutorial into Practical Capacity and Mass Balancing of Lithium Ion Batteries. *J. Electrochem. Soc.* **2017**, *164* (12), A2479–A2486. DOI 10.1149/2.0961712jes.