Supplementary Information (SI) for Sustainable Energy & Fuels.

Supporting Information

A polydihydroxystyrene (PDHS) mussel-mimetic binder: toward sustainable hard carbon electrodes with outstanding performance in sodium-ion batteries

Adrian Beda,[a,b,c,], Jason Beaufrez,[d] Charles Cougnon[d] and Camélia Matei Ghimbeu,[a,b,c,*]

[a] *Université de Haute-Alsace, Institut de Science des Matériaux de Mulhouse (IS2M), CNRS UMR 7361, F-68100 Mulhouse, France*

[b] *Université de Strasbourg, F-67081 Strasbourg, France*

[c] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80039 Amiens Cedex, France*

[d] *Laboratoire MOLTECH-Anjou, Université d'Angers, UMR CNRS 6200, 2 bd Lavoisier, 49045 Angers Cedex, France*

*Corresponding author: camelia.ghimbeu@uha.fr

Experimental part

- **Materials synthesis**

Hard Carbon

Rice starch precursor was purchased from Sigma-Aldrich. The hard carbon (HC) was obtained using the synthesis procedure reported in our previous work.[1] Briefly, the precursor was first dried in an oven under air for 3 days, at 200 °C and then pyrolysed at 1500 °C, under Ar, for one hour. The HC material was used as obtained to prepare electrodes. It has an interlayer spacing, d_{002}, of 3.8 Å, which is large enough to accommodate Na^+. It also has a low BET specific surface area (< 5 m^2 g^{-1} by N_2 and ~ 20 m^2 g^{-1} by CO_2 adsorption) and low active surface area (~ 7 m^2 g^{-1}) which limits electrolyte decomposition and excessive SEI formation. In addition, closed pores are present (7-8%), which is beneficial for high reversible capacity [1,2].

Polydihydroxystyrene (PDHS)

PDHS binder was obtained through demethylation of Polydimethoxystyrene (PDMS) with Boron tribromide (BBr_3).[3] First, PDMS was prepared by reversible-addition-fragmentation chain-transfer (RAFT) polymerization.[4,5] Secondly, PDMS (0.29 g) was dissolved in 18 mL of anhydrous Dichloromethane (DCM) under argon atmosphere. The reaction was cooled to -20 °C before adding BBr_3 (5.34 mL, 0.056 mol). Next, the solution was warmed to room temperature and stirred for 12 h. The crude product was cooled to 0 °C and then treated with water (18 mL). The obtained precipitate was washed with cold water and DCM to obtain polydihydroxystyrene (PDHS, 0.27 mg, 92%). By doing so, a well-defined polymer with a predetermined mass of 58 kg mol^{-1} and a low molar mass dispersity of 1.21 was obtained. Proton NMR spectra of PDHS polymer is shown in Fig. S1.

- **Materials characterisation**

The morphology of the HC-PDHS electrodes was observed by scanning electron microscopy (SEM) using an FEI Quanta 400 microscope equipped with a high-resolution low vacuum field emission gun (FEG).

The HC electrode conductivity was assessed in the absence of the electrolyte using Electrochemical Impedance Spectroscopy (EIS). The electrical resistance of the electrodes was measured, then the electrical conductivity was determined based on the following formula:

$$\sigma = \frac{L}{RA}$$

where, (σ) – electronic conductivity, (L) – electrode length, (R) – electrical resistance and (A) - sectional area of the HC electrode.

XPS analyses on pristine and post-mortem cycled HC electrodes were performed using a VG Scienta SES 2002 spectrometer (Uppsala, Sweden) equipped with a monochromatic Al Kα X-ray source (Al Kα = 1486.6 eV), a hemispherical analyzer (Uppsala, Sweden) and an electron gun to compensate the charging effect. The analyzed zone has a surface of 24 mm^2 and an analysis depth of 9 nm. The electrodes were extracted from the coin cells in the glovebox and washed with DMC, placed on the analysis sample holders, and sealed in an airtight box for transfer to the XPS analysis chamber.

^1H Nuclear Magnetic Resonance (NMR) spectra were recorded using deuterated solvent as internal reference on a BRUKER Advance DRX 500 spectrometer.

- **Materials electrochemical characterisation**

HC-PDHS electrodes were prepared by mixing the HC active material, the conductive carbon black C65 (Imerys) and the PDHS binder (92:05:03) in presence of Et-OH solvent, using a Pulverisette 7 ball mill machine. Electrodes were also prepared using the same ratio (3%) of CMC (Na-carboxymethylcellulose) and PVDF (polyvinylidene fluoride) binders. The obtained slurry was coated on an Aluminum current collector (purchased from S4R), using the doctor blade method, with a gap of 150 µm. Next, round electrodes with a diameter of 11 mm and a mass loading between 2.0 and 2.5 mg cm^{-2} where then punched. Prior to cell assembly, the electrodes were dried in a BUCHI oven at 120 °C under vacuum for 15h.

The coin cells (type CR2032) were assembled in an argon-filled glovebox (H_2O ~ 3 ppm and O_2 < 1 ppm). Sodium metal was used as counter/reference electrode and two glass microfiber separators (Whatman, grade GF/C). The electrolyte used was 1M $NaPF_6$ in ethylene carbonate and dimethyl carbonate (EC:DMC, 1:1 vol.) purchased from E-Lyte. To ensure good repeatability, two cells were assembled for each test.

The electrochemical tests were conducted at room temperature using a Biologic BCS-805 battery cycler. The voltage window considered was 2.1-0.005 V vs. Na^+/Na, and the theoretical capacity of 372 mAh g^{-1} was used to calculate the current density. A galvanostatic step was first performed until 5 mV, then a potentiostatic step was done at 5 mV until the current density reached a value of 3.72 mA g^{-1}. The current was then reversed and a galvanostatic step was performed until 2.1 V. All capacities presented in this paper were determined based only on the HC content of the electrodes.

Results

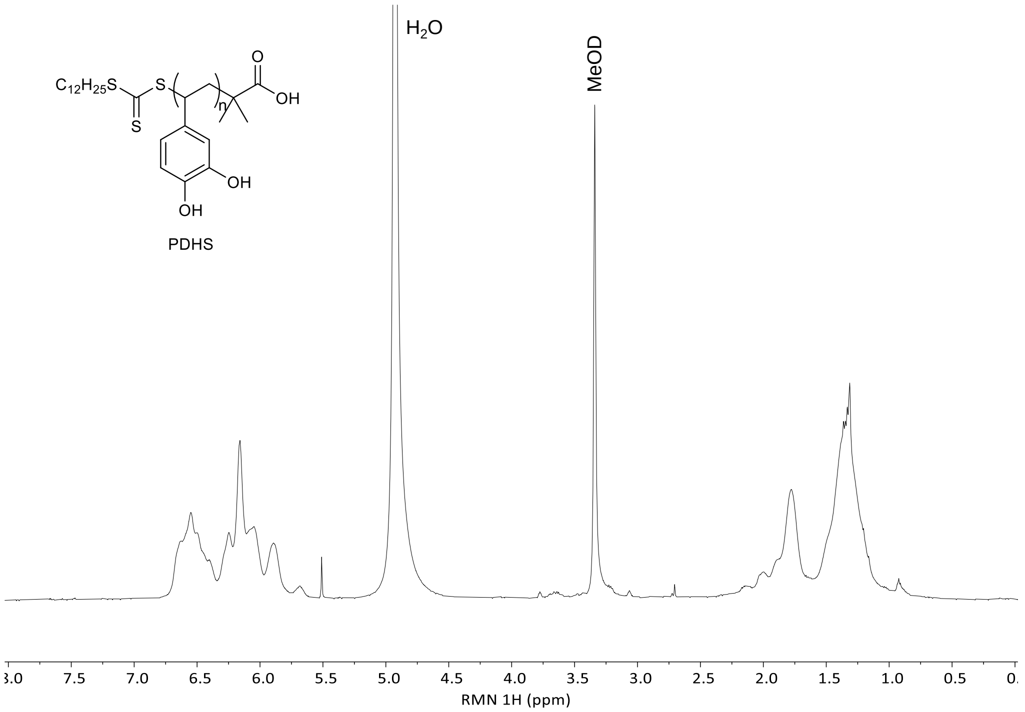

Figure S1: ^{1}H NMR spectrum of PDHS in MeOD solution.

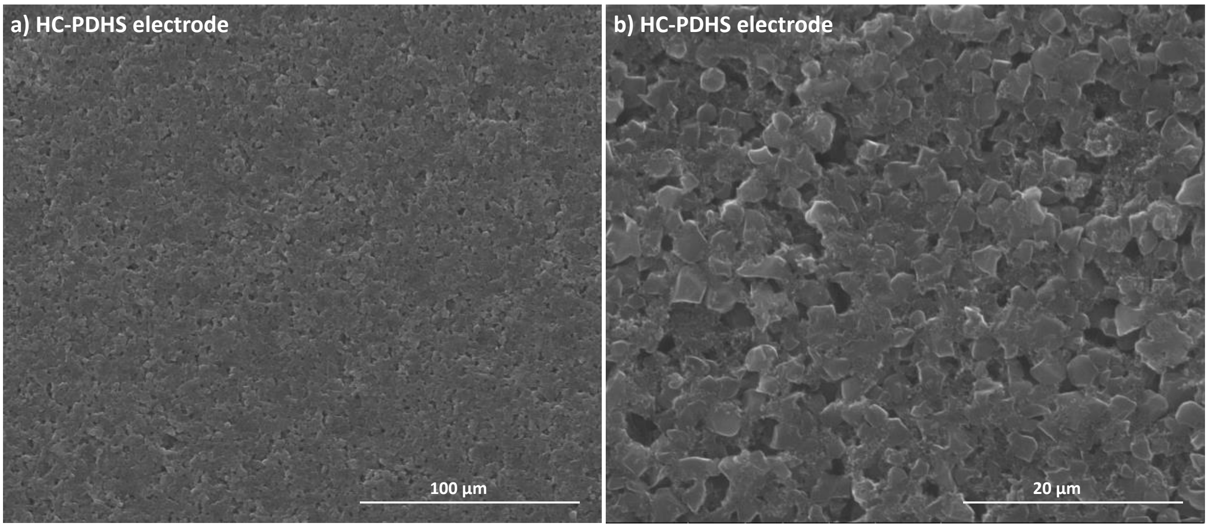

Figure S2*:* SEM images of HC-PDHS electrode at different magnifications: a) 100 µm and b) 20 µm.

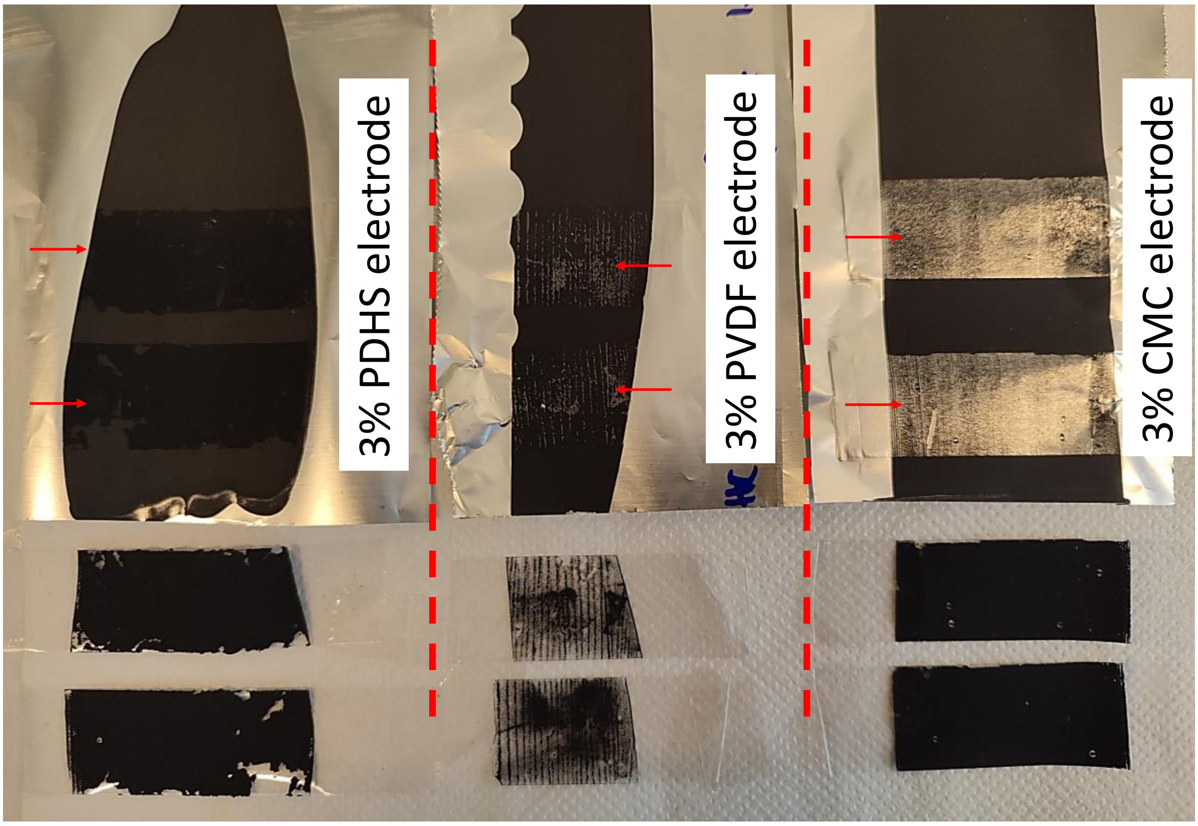

Figure S3: Peel tests performed on the HC electrodes prepared with the three different binders: PDHS, PVDF and CMC.

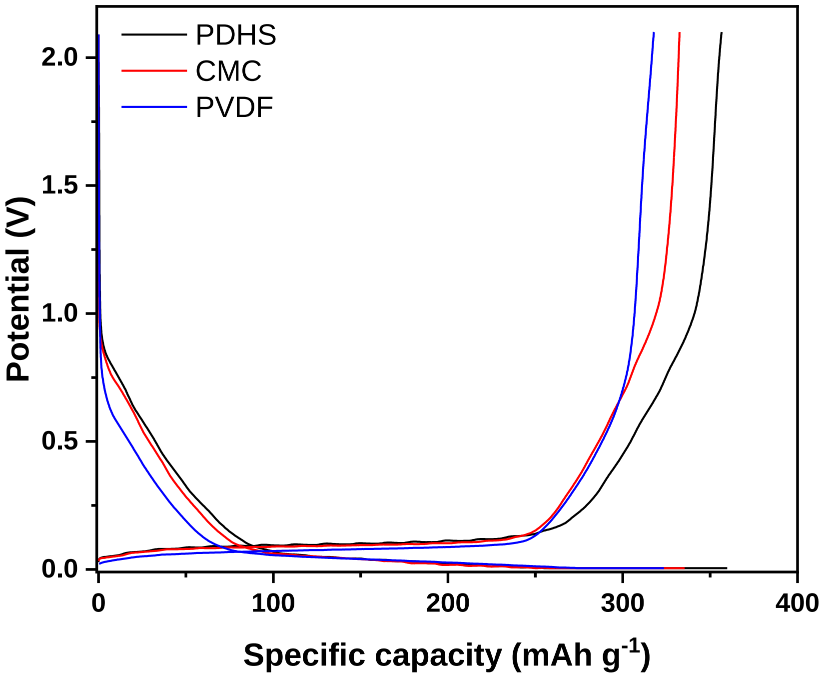

Figure S4: Second discharge-charge cycle of HC electrodes obtained with three different binders: PDHS, CMC and PVDF.

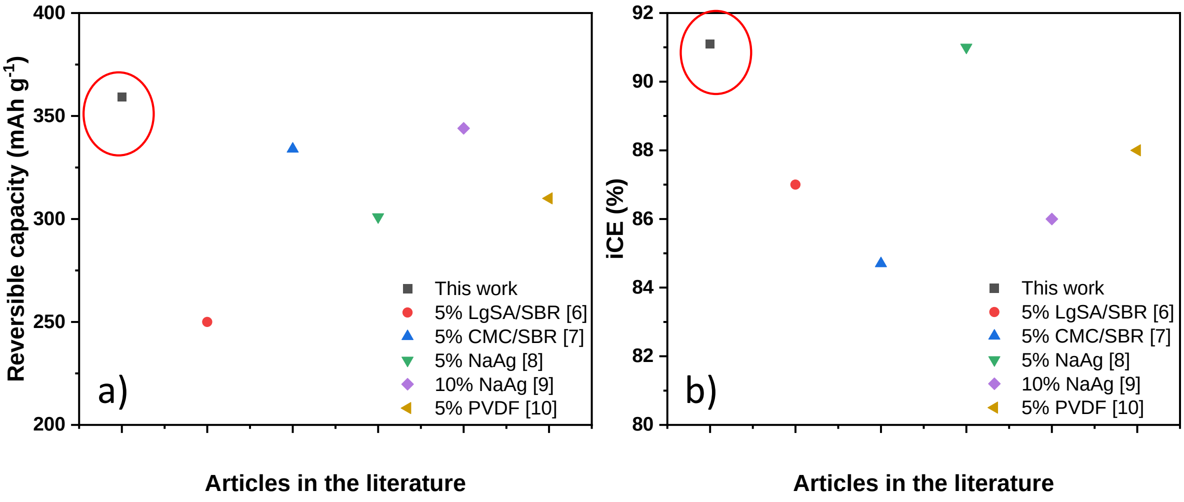

Figure S5: Comparison between PDHS-HC electrode and several selected literature articles [6–10] reporting high performance: a) reversible capacity and b) iCE.

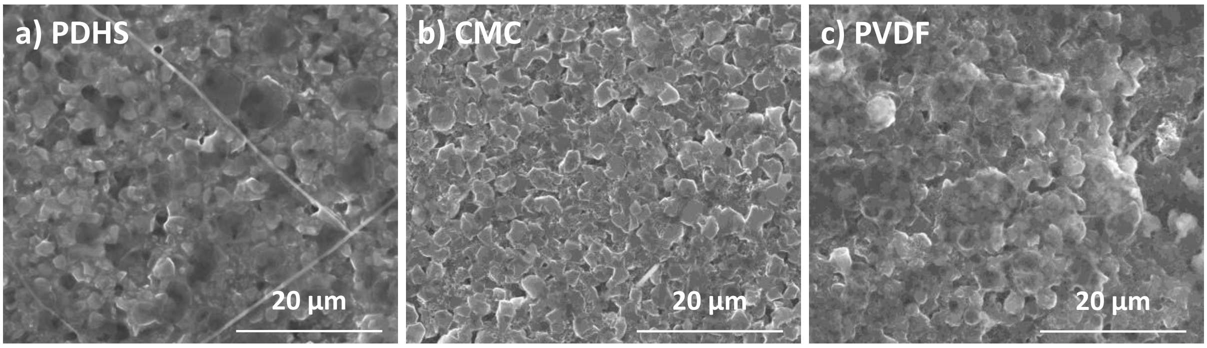

Figure S6: Post-mortem SEM images of the electrodes cycled for five cycles at C/10 rate: a) PDHS, b) CMC and c) PVDF

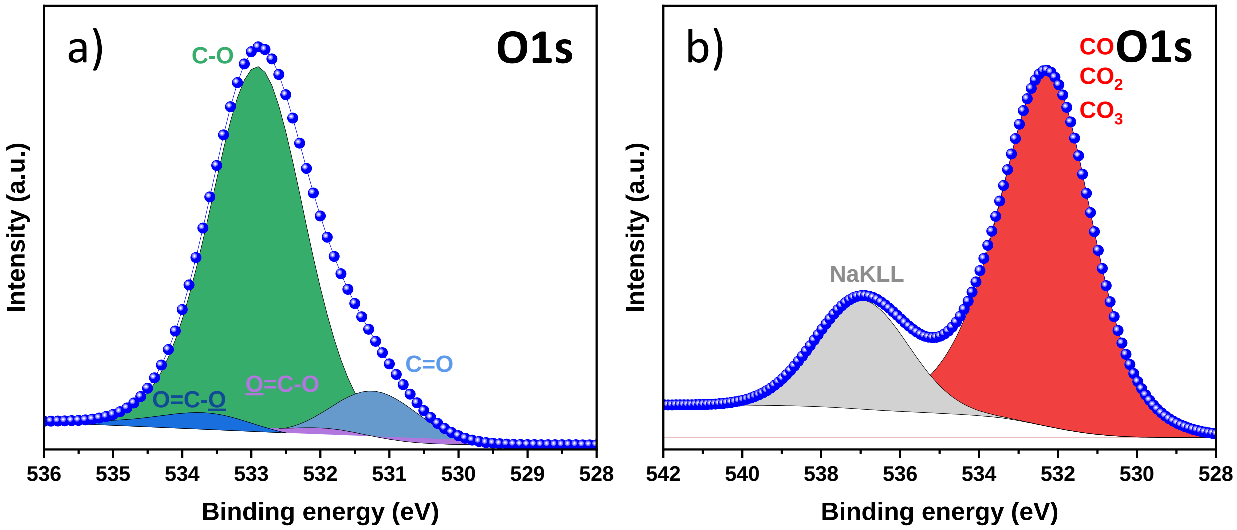

Figure S7: XPS O1s high-resolution deconvoluted spectra of: a) pristine and b) cycled HC-PDHS electrodes.

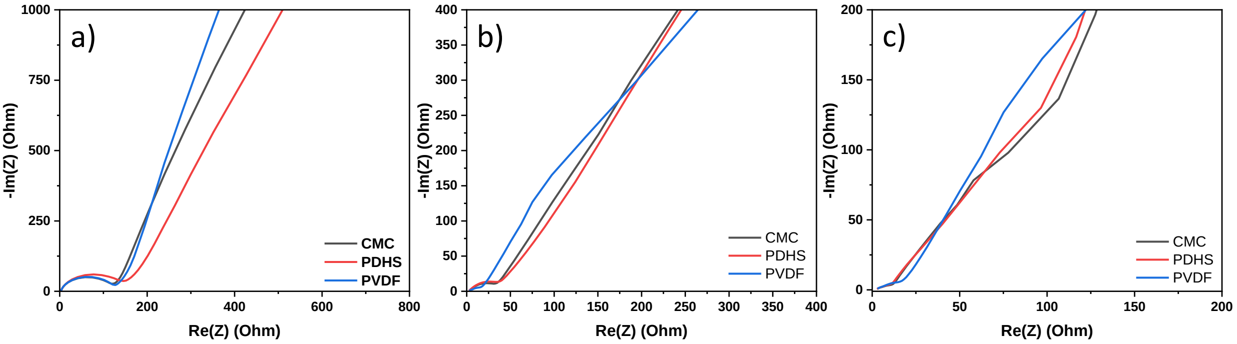

Figure S8: Electrochemical impedance spectroscopy spectra of the three electrodes measured before electrochemical test (a), after cycling the material at C/10 for 5 cycles (b) and after testing the material at 1C rate for another 5 cycles (c).

Table S1: Literature comparison of several electrode materials electrochemical performance (iCE and reversible capacity) showing the different conditions used in term of electrode formulation (binder %) and testing conditions (electrolyte and current density).

Pyrolisis temp. (°C)	Bindert type	Binder (%)	Electrolyte formulation	Current density (mA g^{-1})	iCE (%)	Reversible capacity (mAh g^{-1})	Reference
1500	PDHS	3	1M $NaPF_6$, EC:DMC	37.2	91	360	This work
1500	CMC	3	1M $NaPF_6$, EC:DMC	37.2	90.5	335	This work
1500	PVDF	3	1M $NaPF_6$, EC:DMC	37.2	81	325	This work
1500	PVDF	5	1M $NaPF_6$, EC:DMC	37.2	86	309	[1]
1500	Na-alginate	9	1M $NaPF_6$, EC:DMC	20	87	336	[11]
1400	Na-alginate	5	1M $NaPF_6$, EC:DMC	30	82	254	[12]
1400	CMC	5	1M $NaPF_6$, EC:DMC	30	80	292	[13]
1200	CMC	10	1M $NaClO_4$, EC:DMC	25	66	181	[14]
1300	Polyacrylic acid (PAA)	10	1M $NaClO_4$, EC:DEC	20	86	361	[15]
1300	Polyacrylic acid (PAA)	10	1M $NaClO_4$, EC:DEC (+5% FEC)	20	53	272	[16]
-	CMC/SBR	3	1M $NaPF_6$, EC:DMC	28	92	276	[17]

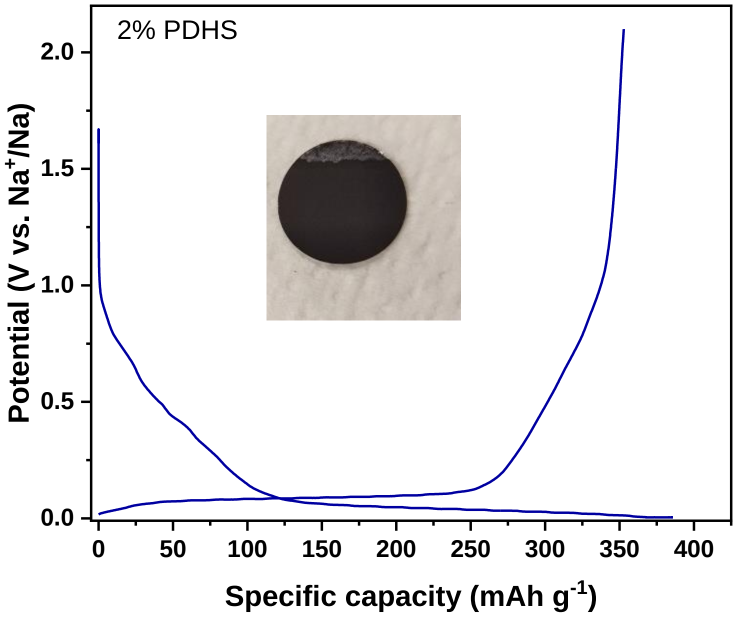

Figure S9*:* First discharge-charge cycle of a PDHS electrode formulated with 2% binder. Inset: example of electrode delamination from Al counter collector observed when working with 2% of PDHS.

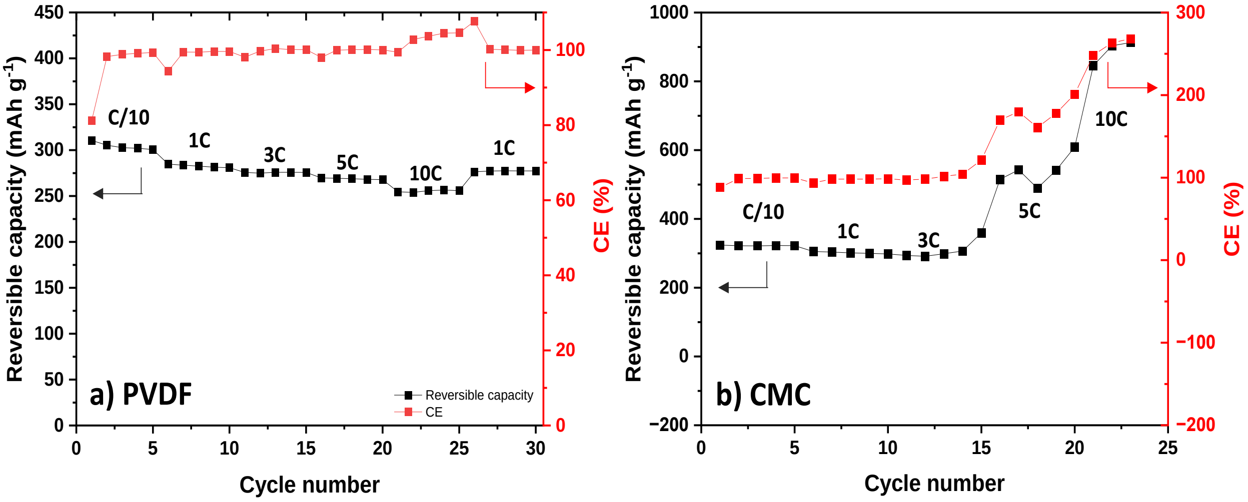

Figure S10*:* Symmetric C-rate tests of the HC electrode prepared with a) PVDF and b) CMC binders.

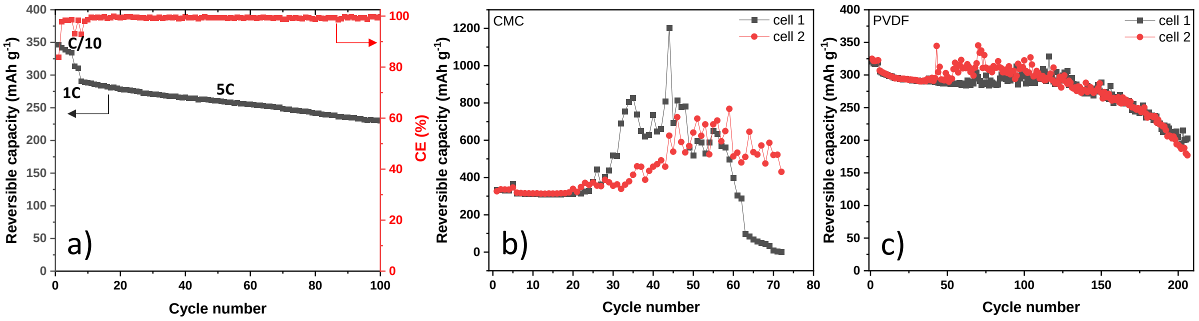

Figure S11*:* a) HC-PDHS electrode cycling behaviour at diffrent C-rates: C/10 (5 cycles), 1C (2 cycles) and 5C (up to 100 cycles). Stability behaviour of CMC (b) and PVDF (c) electrodes at 1C rate, after 5 cycles at C/10.

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