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Electronic Supporting Information

Mechanochemical synthesis of sodium dicarboxylates as anode materials in sodium ion batteries

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All chemicals were used as received and the respective suppliers can be found below.

Chemical	**Abbreviation**	**Supplier**
Sodium acetate anhydrous	NaOAc-d	Sigma-Aldrich
Sodium acetate trihydrate	NaOAc-h	Alfa Aesar
1,4-benzenedicarboxylic acid	BDC	Sigma-Aldrich
2,5-Pyridinedicarboxylic acid	PDC	Sigma-Aldrich
4,4'-biphenyldicarboxylic acid	BPDC	Sigma-Aldrich
4,4'-Stilbenedicarboxylic acid	SDC	TCI
Ethanol	EtOH	VWR
Sodium carboxymethyl cellulose	CMC	Sigma-Aldrich
Sodium alginate	SA	Sigma-Aldrich
Conductive carbon	Super C65	Imerys – Graphite & Carbon

Table S1. Details for mechanochemical experiments, all conducted in a Retsch Mixer Mill MM 400, operated at 30 Hz. All products were dried in an oven at 80 °C directly after milling or after a washing step. Products of highlighted rows were used for electrochemical testing.

BDC (mg)	NaOAc-h (mg)	NaOAc-d (mg)	M/L	Liquid (µL)	η (µL/mg)	Jar (mL)	Balls (mm)	Time (min)	Workup	Yield (mg)
274	**225**	**-**	**1**	**0**	**0.2**	**14**	**2x7**	**60**	**-**	0.288
249	255	-	1.25	0	0.2	14	2x7	60	-	0.266
225	276	-	1.5	0	0.2	14	2x7	60	-	0.239
191	313	-	2	0	0.25	14	2x7	90	-	0.204
145	356	-	3	0	0.3	14	2x7	60	-	0.166
129	371	-	3.5	0	0.3	14	2x7	90	-	0.208
117	383	-	4	0	0.3	14	2x7	60	-	0.175
335	-	165	1	0	0	25	2x12	240	-	n.d.
1005	-	496	1	0	0	14	2x7	90	-	n.d.

BPDC (mg)	NaOAc-h (mg)	NaOAc-d (mg)	M/L	Liquid (µL)	η (µL/mg)	Jar (mL)	Balls (mm)	Time (min)	Workup	Yield (mg)
374	-	127	1	250 (H2O)	0.5	14	2x7	60	-	0.349
297	-	202	2	250 (H2O)	0.5	14	2x7	60	-	0.280
297	-	202	2	250 (EtOH)	0.5	14	2x7	60		0.421
249	-	252	3	250 (H2O)	0.5	14	2x7	60	-	0.385
249	**-**	**252**	**3**	**250 (EtOH)**	**0.5**	**14**	**2x7**	**60**	**EtOH**	0.420
213	-	288	4	250 (EtOH)	0.5	14	2x7	60	-	0.352

SDC (mg)	NaOAc-h (mg)	NaOAc-d (mg)	M/L	Liquid (µL)	η (µL/mg)	Jar (mL)	Balls (mm)	Time (min)	Workup	Yield (mg)
383	-	117	1	250 (H2O)	0.5	14	2x7	60	-	0.359
239	161	-	1.3	0	0.2	14	2x7	15	-	0.239
199	201	-	2	0	0.2	14	2x7	15	-	0.211
248	**252**	**-**	**2**	**120 (H2O)**	**0.5**	**14**	**2x7**	**60**	**EtOH**	0.252
261	-	239	3	250 (H2O)	0.5	14	2x7	60	-	0.343
225	-	275	4	250 (EtOH)	0.5	14	2x7	60	-	0.354

PDC (mg)	NaOAc-h (mg)	NaOAc-d (mg)	M/L	Liquid (µL)	η (µL/mg)	Jar (mL)	Balls (mm)	Time (min)	Workup	Yield (mg)
335	-	165	1	250 (EtOH)	0.5	14	2x7	60	-	0.352
208	192	-	1.1	0	0.2	14	2x7	60	-	0.191
202	-	198	2	0	0	14	2x7	15	-	0.250
152	248	-	2	0	0.25	14	2x7	60	-	0.142
152	248	-	2	103 (H2O)	0.5	14	2x7	60	-	0.165
152	**248**	**-**	**2**	**103 (EtOH)**	**0.5**	**14**	**2x7**	**60**	**-**	0.143
202	-	298	3	250 (EtOH)	0.5	14	2x7	60	-	0.249

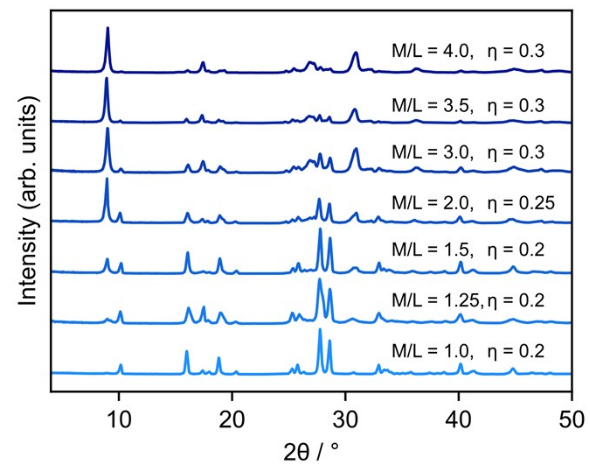

Figure S1. PXRD patterns (normalised) of the mechanochemical product of sodium acetate and BDC in various metal-linker ratios (M/L), employing 30 Hz and using 14 mL jars with two 1.3 g (7 mm diameter) stainless steel balls.

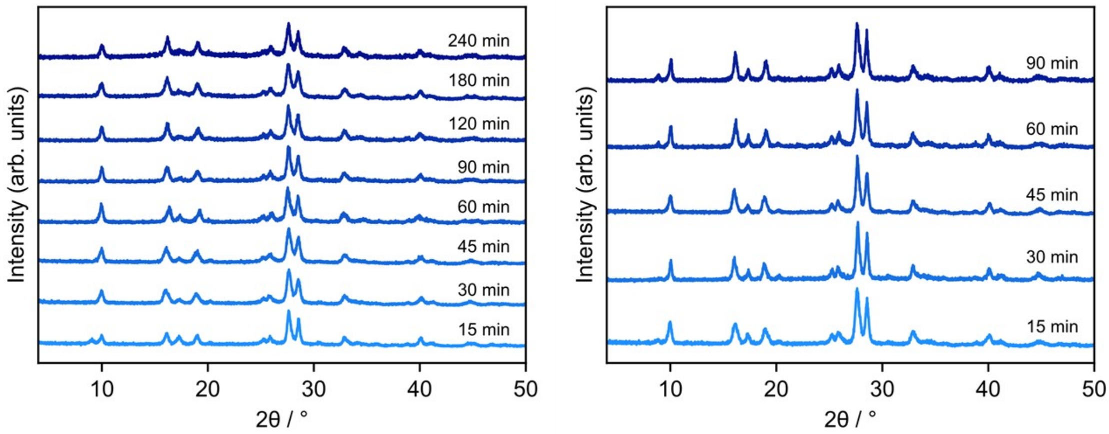

Figure S2. PXRD patterns (normalised) of the mechanochemical product of sodium acetate and BDC (ratio of 1:1) without liquid, employing 30 Hz. Experiments using 14 mL jars with two 1.3 g (7 mm diameter) stainless steel balls (*left*) and experiments using 25 mL jars with two 7 g (12 mm diameter) stainless steel balls (right)

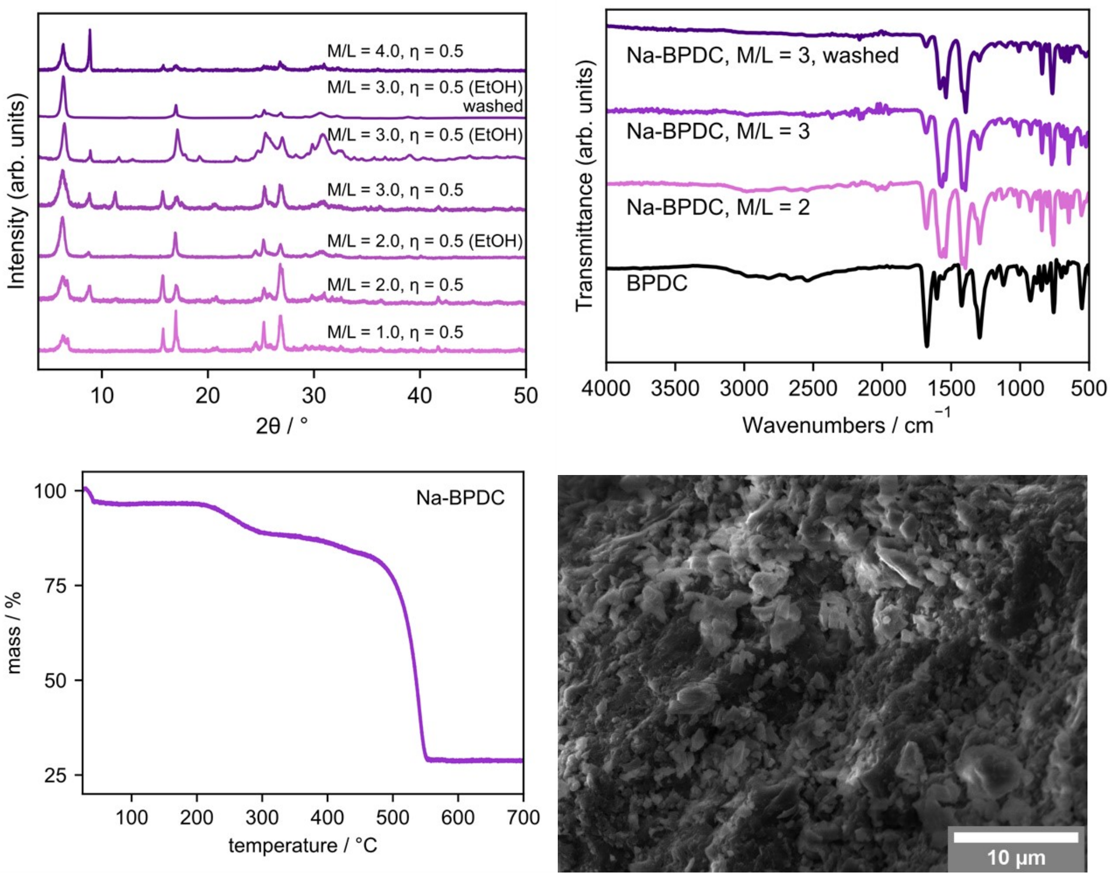

Figure S3. Characterisation of mechanochemically synthesised Na-BPDC. PXRD patterns (normalised) of the mechanochemical product of sodium acetate and BPDC in various metal-linker ratios (M/L), employing 30 Hz and using 14 mL jars with two 1.3 g (7 mm diameter) stainless steel balls (*top left*); FTIR spectra of selected samples (*top right*); TGA profile (*bottom left*) and SEM image (*bottom right*) of Na-BPDC sample used for electrochemical testing (M/L=3, washed).

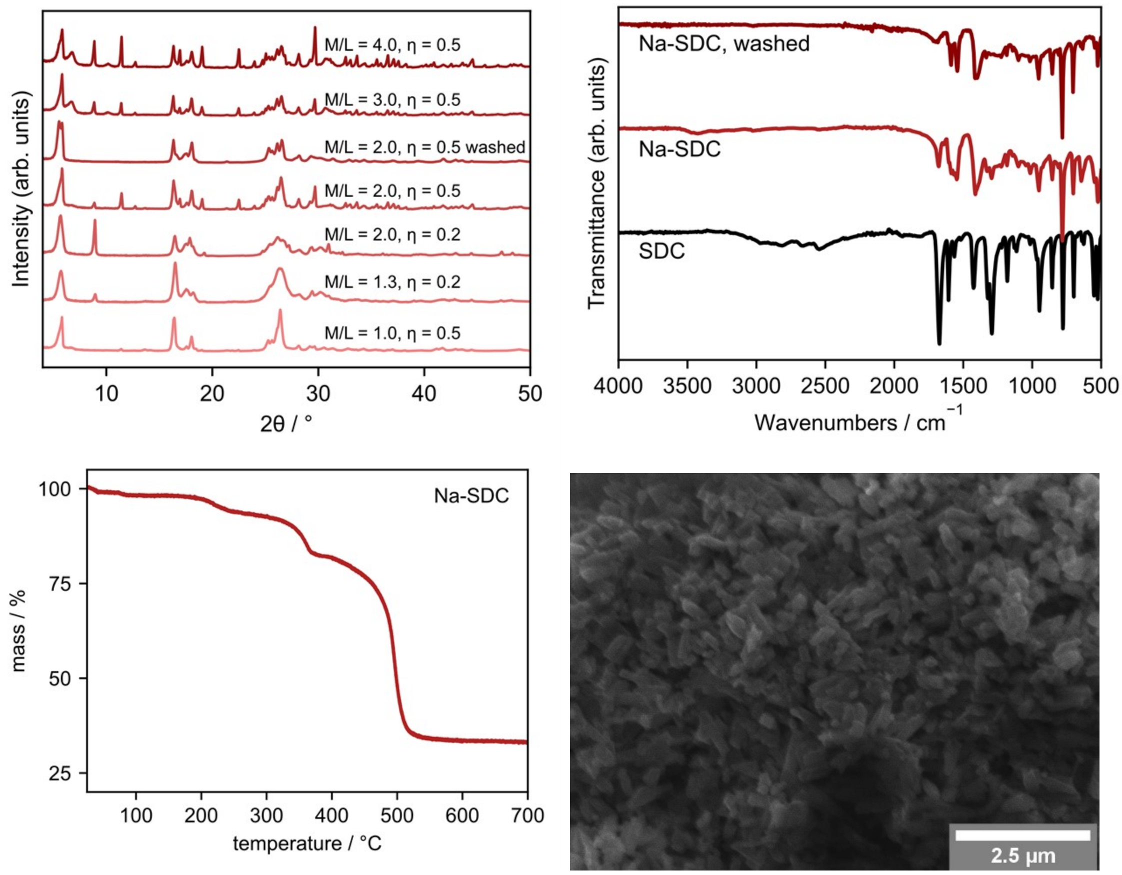

Figure S4. Characterisation of mechanochemically synthesised Na-SDC. PXRD patterns (normalised) of the mechanochemical product of sodium acetate and SDC in various metal-linker ratios (M/L), employing 30 Hz and using 14 mL jars with two 1.3 g (7 mm diameter) stainless steel balls (*top left*); FTIR spectra of selected samples (*top right*); TGA profile (*bottom left*) and SEM image (*bottom right*) of Na-SDC sample used for electrochemical testing (M/L=2, washed).

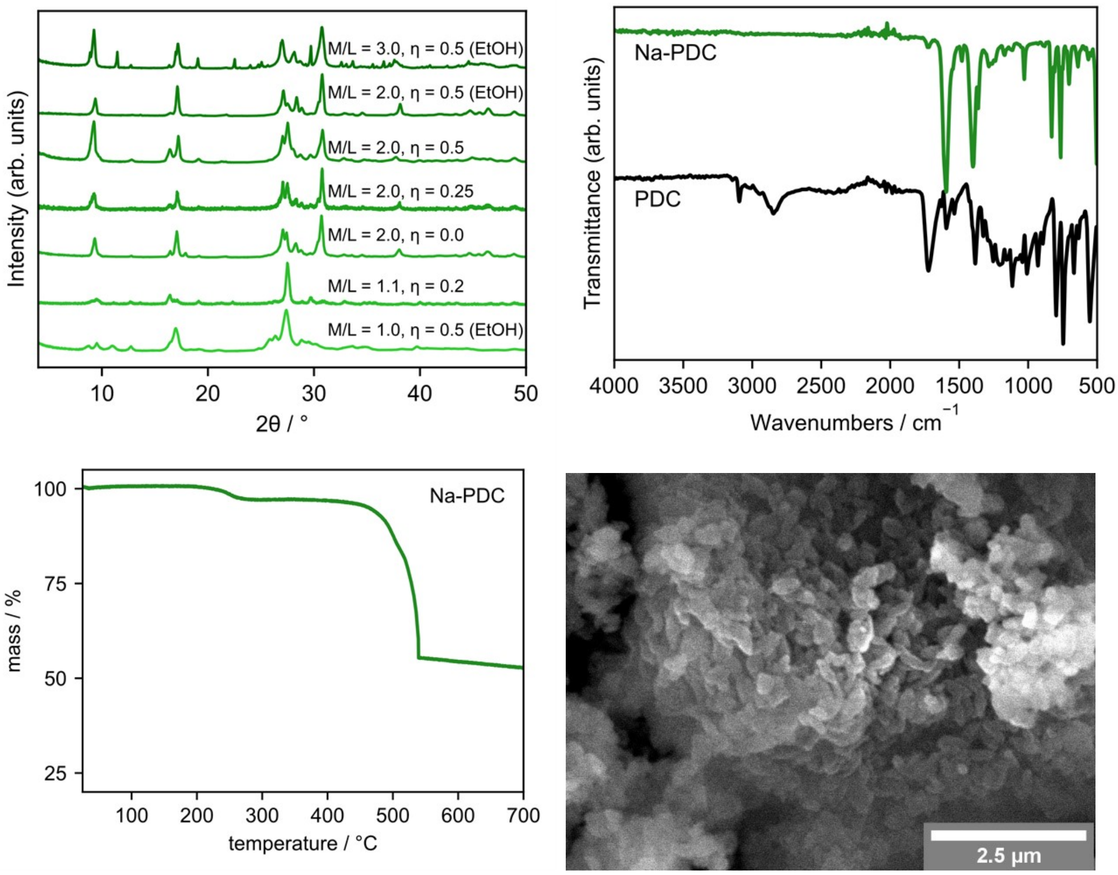

Figure S5. Characterisation of mechanochemically synthesised Na-PDC. PXRD patterns (normalised) of the mechanochemical product of sodium acetate and PDC in various metal-linker ratios (M/L), employing 30 Hz and using 14 mL jars with two 1.3 g (7 mm diameter) stainless steel balls (*top left*); FTIR spectra of selected samples (*top right*); TGA profile (*bottom left*) and SEM image (*bottom right*) of Na-PDC sample used for electrochemical testing (M/L=2, EtOH).

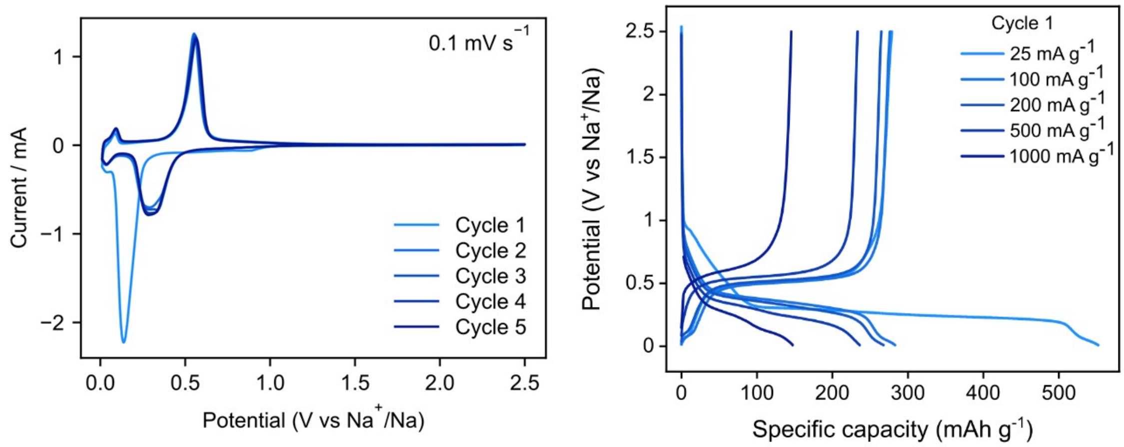

Figure S6. CV profile for Na-BDC at a scan rate of 0.1 mV s^{-1} (*left*) and charge/discharge curves from rate capability for 1st cycle at different current densities (*right*).

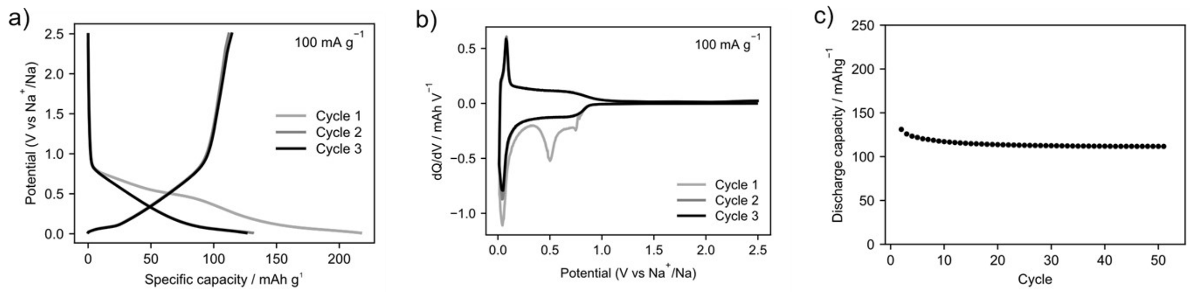

Figure S7. a) Galvanostatic charge/discharge profile and b) differential capacity plot for the first three cycles of an electrode prepared using Super C65 (90%) and CMC (10%) and cycled between 0.01–2.5 V at 100 mA g^{-1}. c) Discharge capacity of the electrode over 50 cycles. The discharge capacity stabilises at ~112 mAh g^{-1}, which would correspond to a maximum capacity contribution of 37.3 mAh g^{-1} for electrodes prepared with 30% conductive carbon (Super C65).

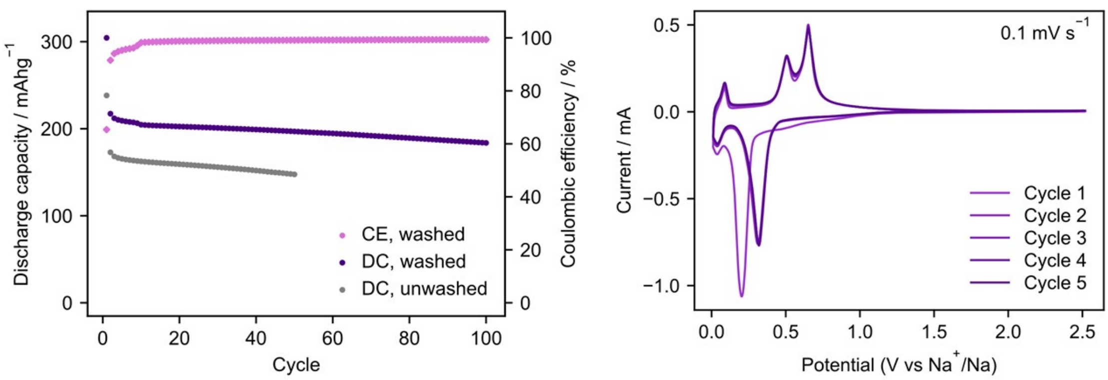

Figure S8. Discharge capacity (DC) for unwashed Na-BPDC (50 cycles) and DC and Coulombic efficiency (CE) for washed Na-BPDC (100 cycles) measured at 100 mAh g^{-1} in a voltage window of 0.01–2.5 V for both samples (*left*) and CV profile for Na-BPDC at scan rate of 0.1 mV s^{-1} (*right*).

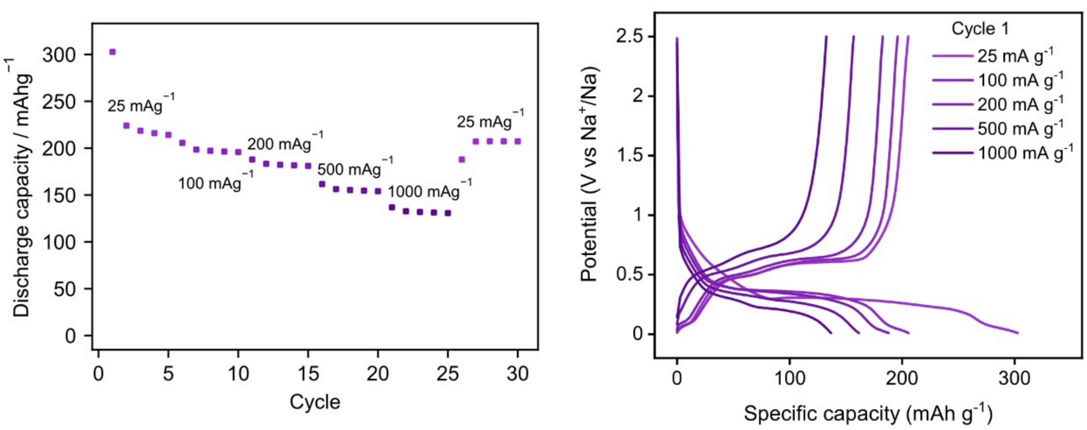

Figure S9. Rate performance for Na-BPDC at different current rates, where cycling was carried out 5 times at each step in a voltage window of 0.01–2.5 V (*left*) and corresponding charge/discharge profiles for 1st cycle at different current densities (*right*).

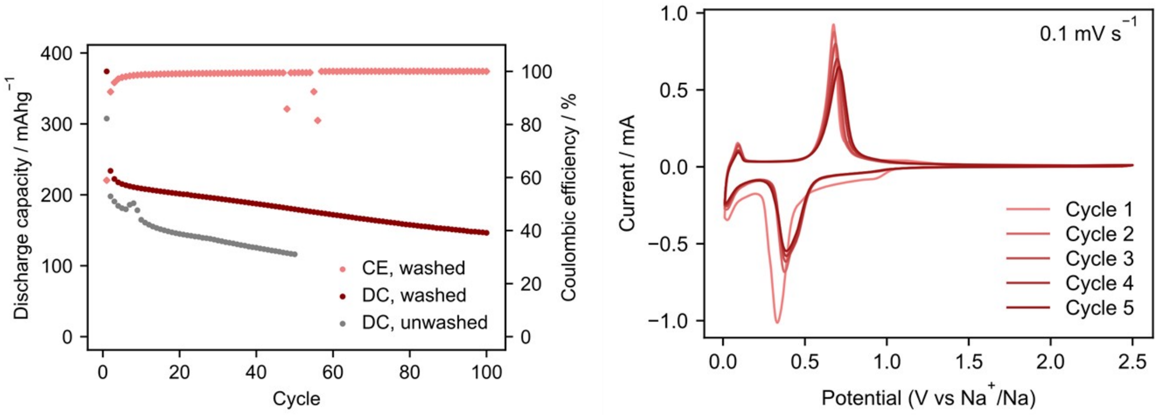

Figure S10. Discharge capacity (DC) for unwashed Na-SDC (50 cycles) and DC and Coulombic efficiency (CE) for washed Na-SDC (100 cycles) measured at 100 mAh g^{-1} in a voltage window of 0.01–2.5 V for both samples (*left*) and CV profile for Na-SDC at scan rate of 0.1 mV s^{-1} (*right*).

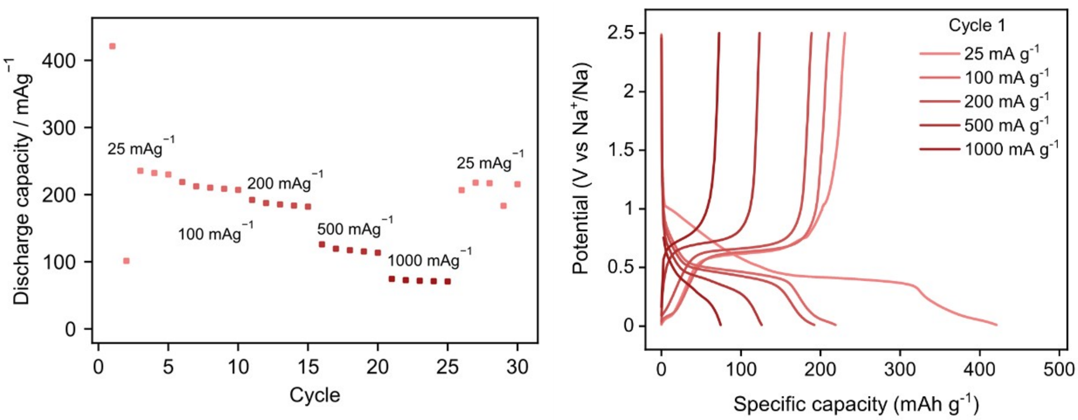

Figure S11. Rate performance for Na-SDC at different current rates, where cycling was carried out 5 times at each step in a voltage window of 0.01–2.5 V (*left*) and corresponding charge/discharge curves for 1st cycle at different current densities (*right*).

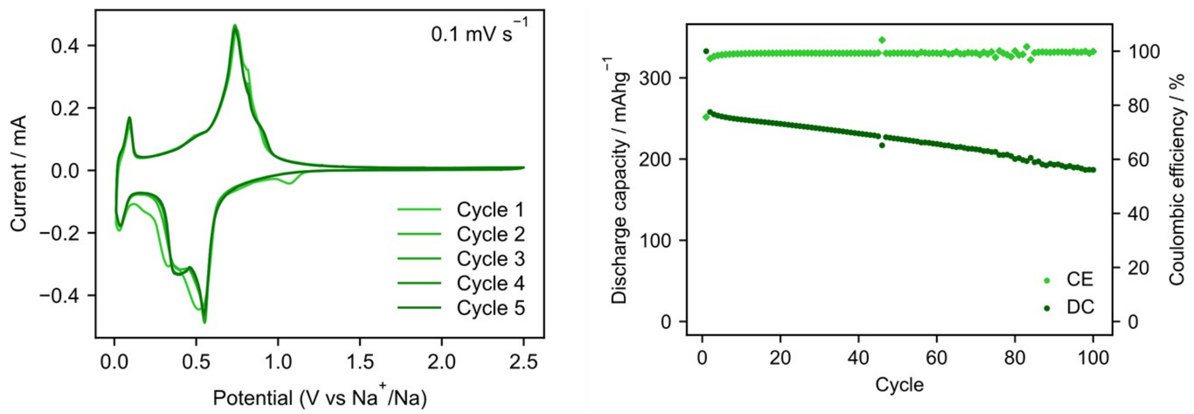

Figure S12. CV profile for Na-PDC at scan rate of 0.1 mV s^{-1} (*left*) and discharge capacity (DC) and Coulombic efficiency (CE) for Na-PDC at current density of 100 mAh g^{-1}, cycled between 0.01–2.5 V (*right*).

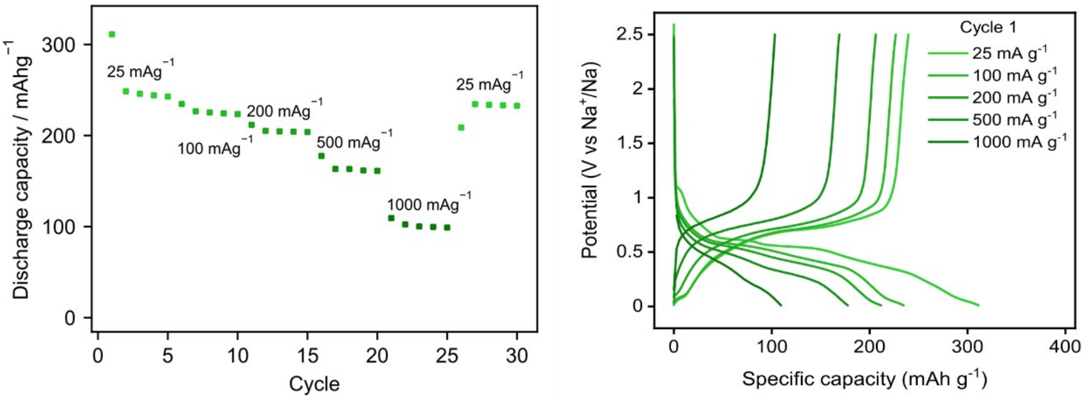

Figure S13. Rate performance for Na-PDC at different current rates, where cycling was carried out 5 times at each step in a voltage window of 0.01–2.5 V (*left*) and corresponding charge charge/discharge profiles for 1st cycle at different current densities (*right*).

Table S2. Brief comparison of electrochemical properties for the materials synthesised from solution and by mechanochemical methods. The value denoted with an asterisk (*) is not explicitly mentioned in the referenced article but estimated from the plot shown in the publication.

Synthesis method	**Binder**	**Electrode composition** (active: conductive carbon: binder)	**Galvanostatic cycling performance** Discharge capacity, rate, cycle number	**Reference**
Na-BDC				
Mechanochemical	CMC	60:30:10	230 mA h g^{-1}, 100 mA g^{-1}, 100	This work
Solution (RT - EtOH) – NaHBDC	Sodium alginate	50:35:15 or 60:30:10	244 mA h g^{-1}, 20 mA g^{-1} 50	[1]
Na-BPDC				
Mechanochemical	CMC	60:30:10	184 mA h g^{-1}, 100 mA g^{-1}, 100	This work
Solution (H_2O-EtOH) – Na_2BPDC	CMC	57.1:28.6:14.3	~190-200 mA h g^{-1},* 20.3 mA g^{-1}, 150	[2]
Na-SDC				
Mechanochemical	CMC	60:30:10	146 mA h g^{-1}, 100 mA g^{-1}, 100	This work
Solution (RT - EtOH) – Na_2SDC	CMC	50:40:10	204 mA h g^{-1}, 50 mA g^{-1}, 50	[3]
Na-PDC				
Mechanochemical	CMC	60:30:10	187 mA h g^{-1}, 100 mA g^{-1}, 100	This work
Solution (Reflux – water and EtOH) – Na_2PDC	PVDF	50:35:15	225 mA h g^{-1}, 25.4 mA g^{-1}, 100	[4]

References:

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