

# Understanding the electrochemical behaviour of reduced graphene oxide cathodes in all-carbon Na-ion batteries

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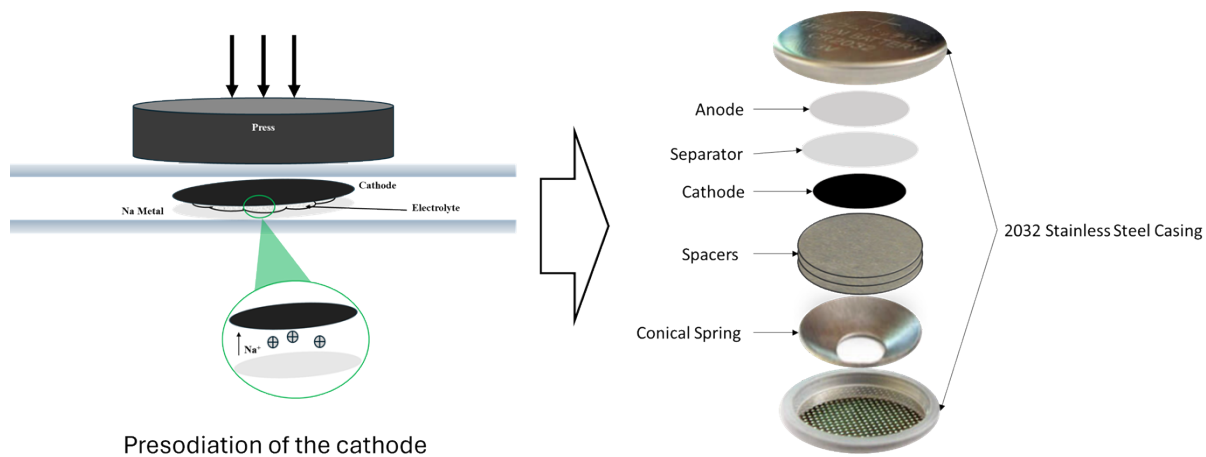
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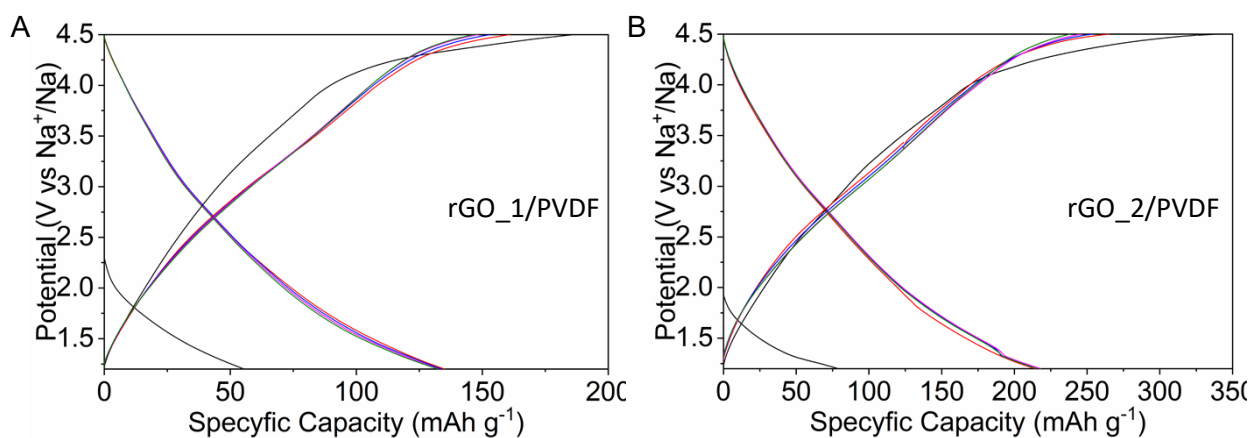
**Table S1** Parameters derived from fitting Raman spectra of raw rGO powders

		rGO_1	rGO_2	Comment
<b>Band D</b>	Position	1348.2	1348.8	Breathing mode of $A_{1g}$ symmetry resulting from various defects and basal edges.
	FWHM	102.4	115.1	
<b>Band G</b>	Position	1591.1	1597.1	$E_{2g}$ symmetry in-plane bond-stretching motion of $sp^2$ pairs of C atoms – ideal graphitic.
	FWHM	60.1	60.6	
<b>Band D'</b>	Position	1616.4	1619.0	$E_{2g}$ symmetry attributed to disorder in graphitic surface layer.
	FWHM	36.6	35.9	
<b>Band A</b>	Position	1530.2	1543.1	Amorphous carbon. FWHM $\propto 1/\text{crystallinity}$
	FWHM	124.9	129.0	
<b>Band D*</b>	Position	1096.8	1103.2	Defect mode in graphitic lattice provided by $sp^2$ – $sp^3$ bonds at the edges of graphene.
	FWHM	103.4	98.5	
$I_D/I_G$		1.45	1.50	$\propto$ defects concentration
$I_{D'}/I_G$		0.40	0.33	$\propto$ defects on graphitic surface layer
$I_A/I_G$		0.31	0.33	$\propto$ decrease of crystallinity
$I_{D^*}/I_G$		0.17	0.18	$\propto$ $sp^3$ bonds on the edges

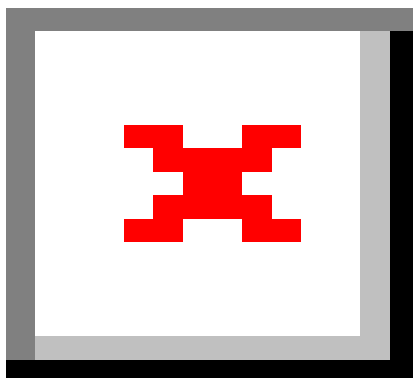
FWHM – Full Width at Half Maximum.



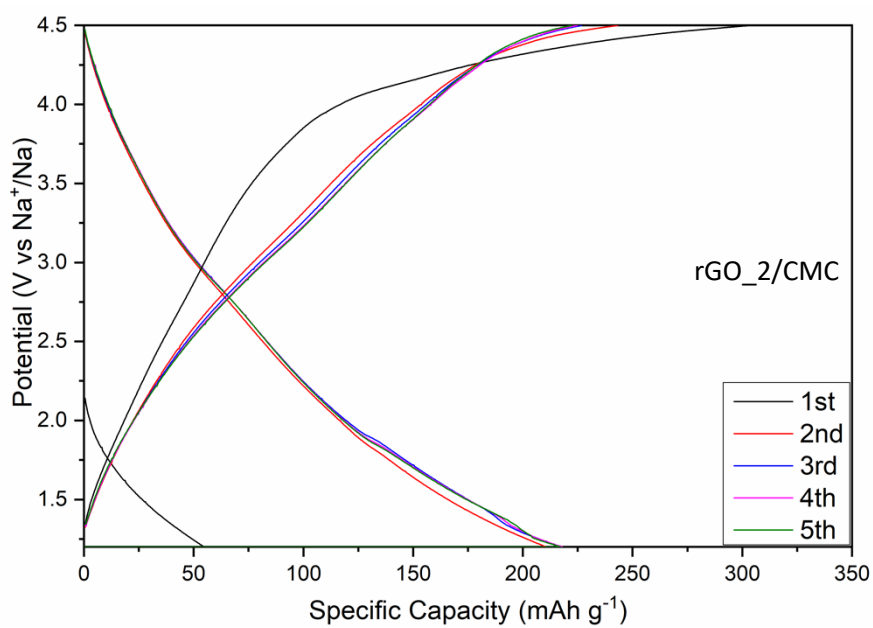
**Fig. S1** Schematic of full cell assembly with presodiation step via direct contact short circuit method.



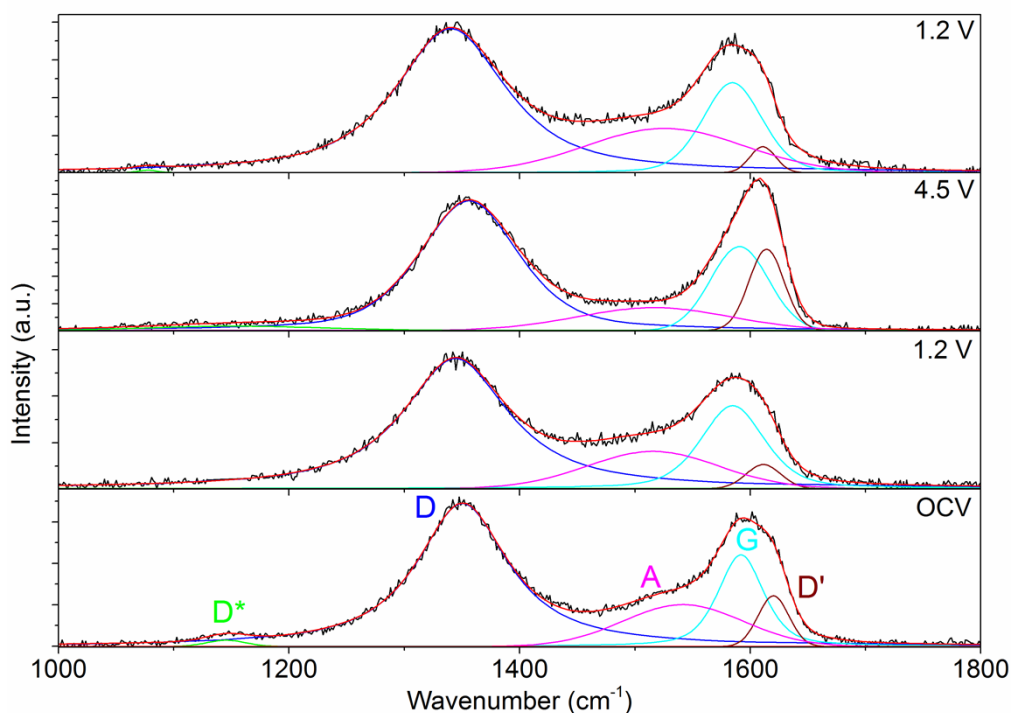
**Fig. S2** Potential profiles of the first five cycles of (a) rGO\_1/PVDF and (b) rGO\_2/PVDF cathodes.



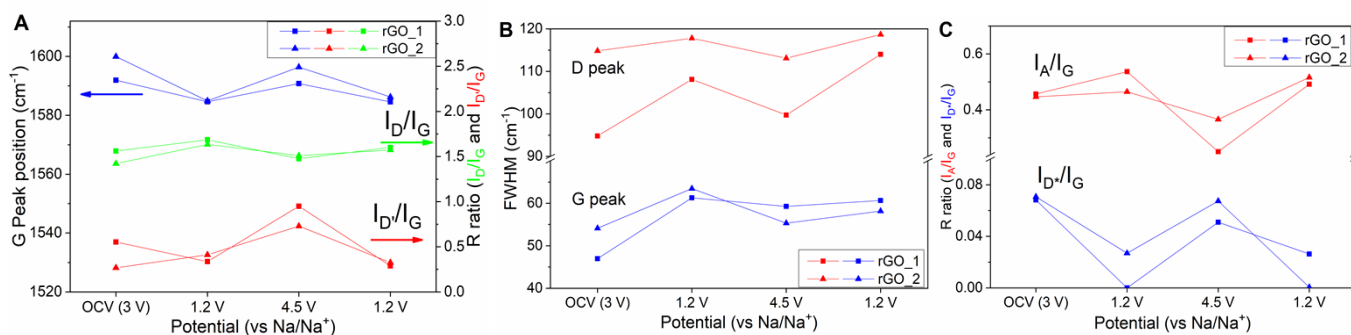
**Fig. S3** *Ex situ* XRD patterns of rGO\_1 and rGO\_2 electrodes. Black dots indicate peaks of rGO. Blue and green dots indicate NaCl and Al peaks respectively. Al peaks come from the current collector.



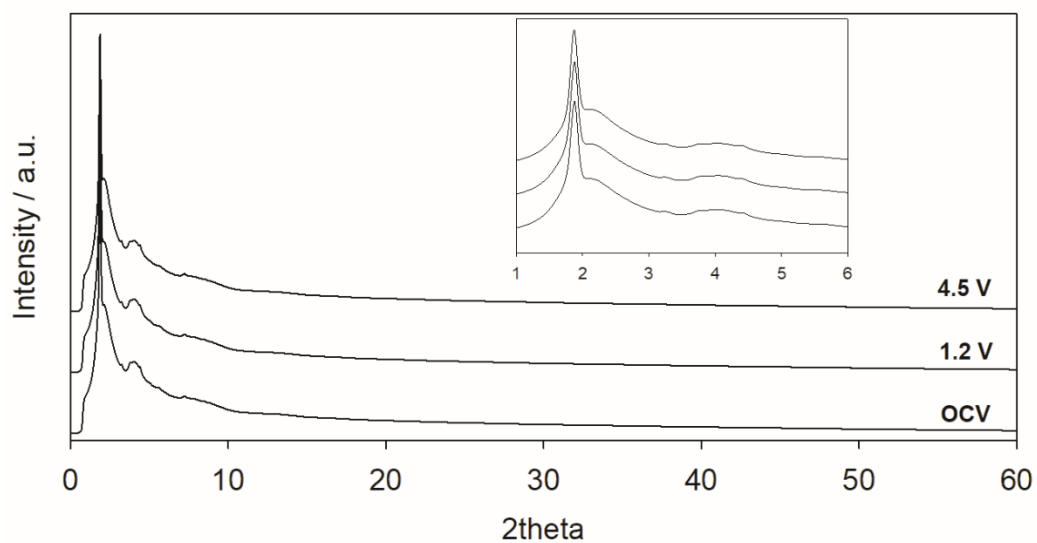
**Fig. S4** Potential profiles of the first five cycles of rGO<sub>2</sub>/CMC cathode.



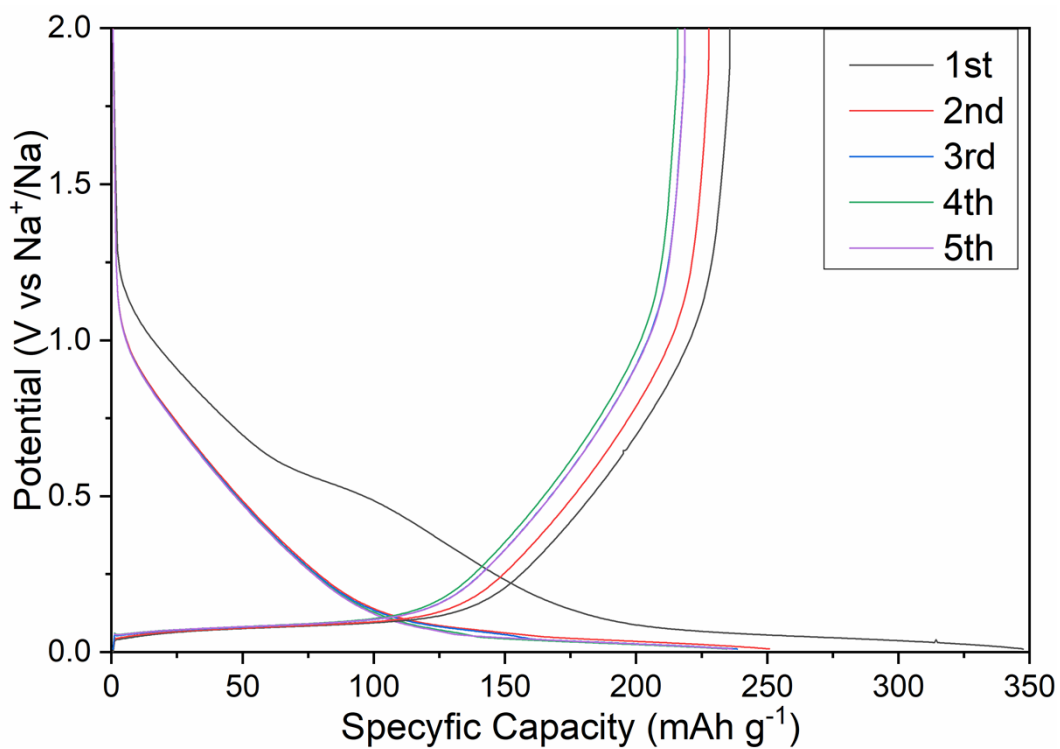
**Fig. S5** Fitted *in situ* Raman spectra of rGO\_1 cathode at OCV and cut off potentials. The extracted data is presented in Fig. 5 in the main text.



**Fig. S6** Data derived from fitted peaks of *in situ* Raman spectra at cut off potentials. (a) The position of G peaks (blue), the D/G intensity ratios (green) and D'/G intensity ratios (red) at key potentials of CV. (b) The full width at half maximum (FWHM) of D (red) and G (blue) peaks at key potentials of CV. (c) The A/G peaks intensity ratios (red) and D\*/G peaks intensity ratios (blue) at key potentials of CV.



**Fig. S7** Experimental diffractions patterns of rGO\_2 collected at OCV, 1.2 V and 4.5 V. No significant variation is observed. The inset highlights the low angle region where the main signal, coming from the empty cell, is observed.



**Fig. S8** Potential profiles of the first three cycles of hard carbon negative electrode in half cell vs Sodium in 1M NaClO<sub>4</sub> in EC:PC electrolyte.