Supporting Information

Can Solvothermal Synthesis Drive Defectivity and Unlock Better Electrochemical Performance in Li-Rich Layered Oxides?

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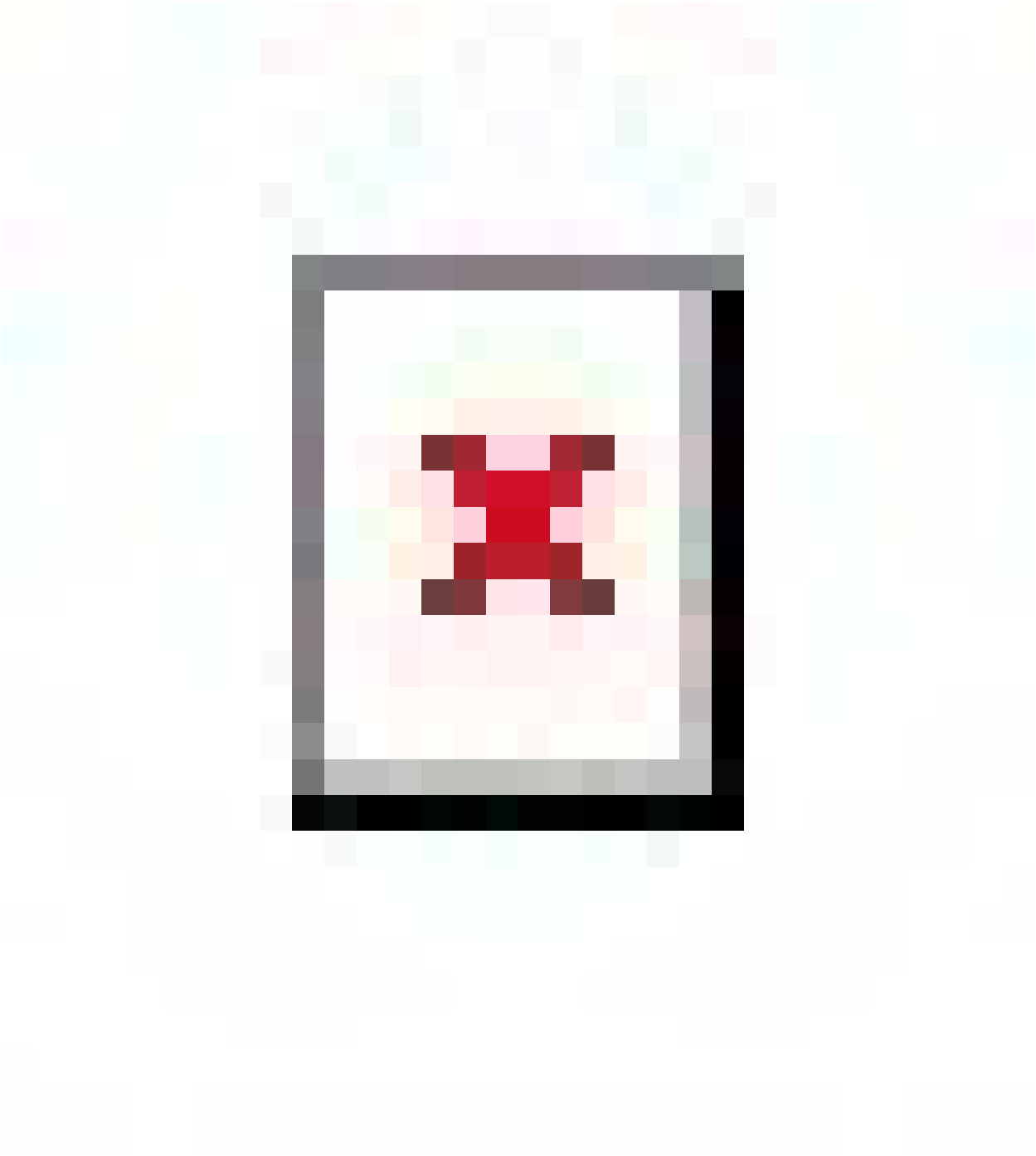

Figure S1. Diffraction patterns acquired for the precursors and corresponding reference patterns.

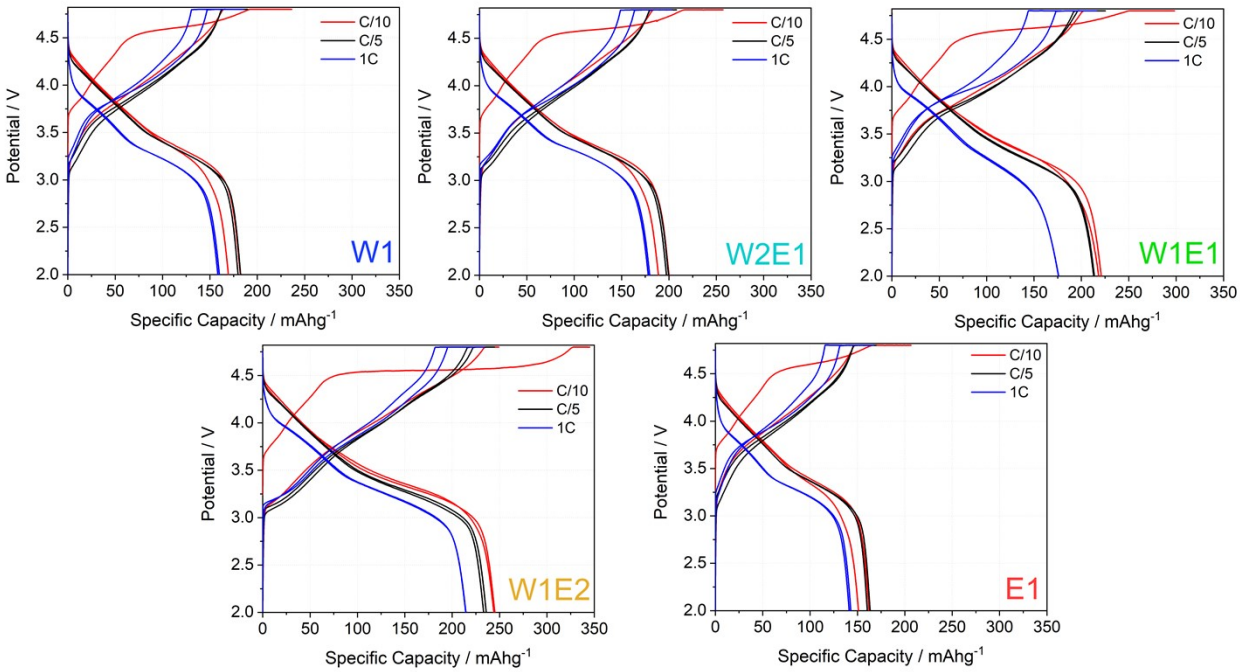

Figure S2. Charge/discharge cycles obtained for all the samples applying the formation procedure before galvanostatic cycling at C/10.

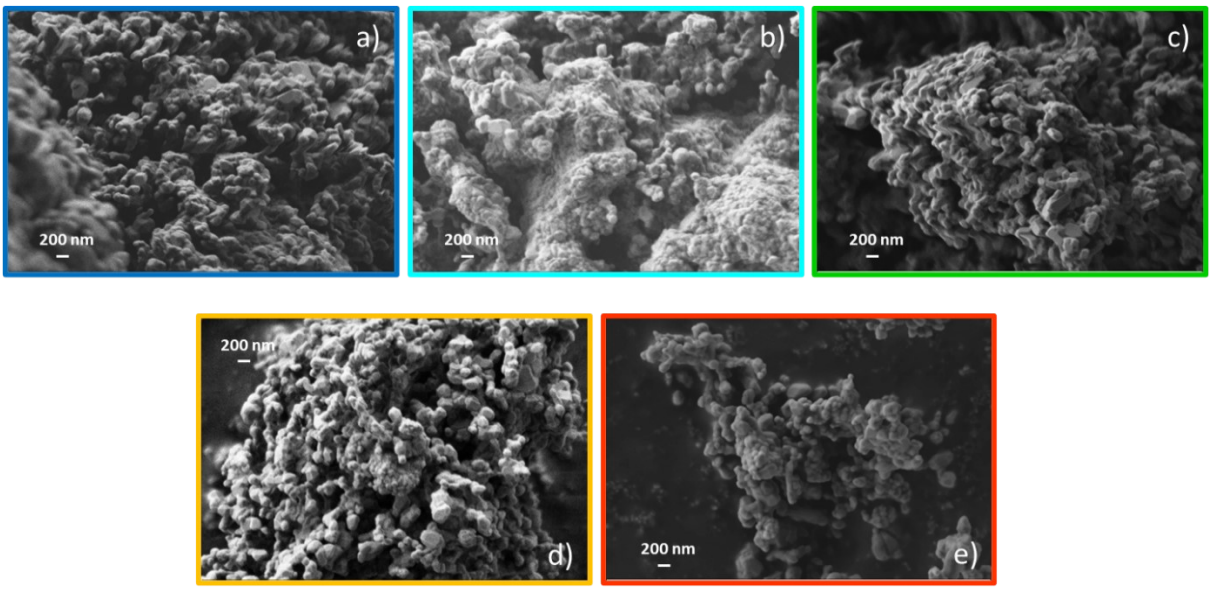

Figure S3. SEM images of a) W1, b) W2E1, c) W1E1, d) W1E2 and e) E1 samples.

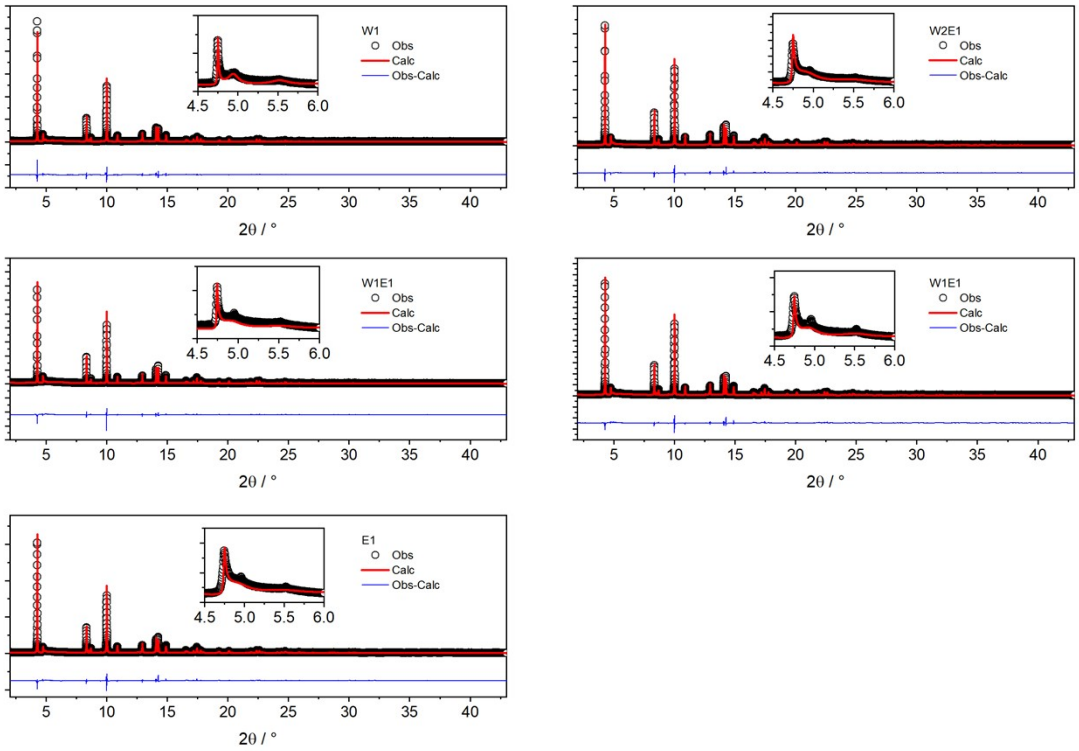

Figure S4. Rietveld refinement of the XRD patterns of W1, W2E1, W1E1, W1E2 and E1 using the FAULTS software.

Table S1: Rietveld refined parameters for C2/m.					
Sample	**W1**	**W2E1**	**W1E1**	**W1E2**	**E1**
Atomic position and occupancies (Wycoff position; OF=occupancy fraction)					
Lithium ion layer	(2c) (0 0 ½) OF(Li)=1	(2c) (0 0 ½) OF(Li)=1	(2c) (0 0 ½) OF(Li)=1	(2c) (0 0 ½) OF(Li)=1	(2c) (0 0 ½) OF(Li)=1
	(4h) (0 0.661 ½) OF(Li)=1	(4h) (0 0.661 ½) OF(Li)=1	(4h) (0 0.661 ½) OF(Li)=1	(4h) (0 0.661 ½) OF(Li)=1	(4h) (0 0.661 ½) OF(Li)=1
Metal ions blend layer	(2b) (0 ½ 0) OF(Li)=0.645 OF(Mn)=0.355	(2b) (0 ½ 0) OF(Li)=0.653 OF(Mn)=0.347	(2b) (0 ½ 0) OF(Li)=0.59 OF(Mn)=0.41	(2b) (0 ½ 0) OF(Li)=0.65 OF(Mn)=0.35	(2b) (0 ½ 0) OF(Li)=0.675 OF(Mn)=0.325

	(4g) (0 0.169 0) OF(Mn)=0.925 OF(Li)=0.075	(4g) (0 0.169 0) OF(Mn)=0.933 OF(Li)=0.067	(4g) (0 0.169 0) OF(Mn)=0.87 OF(Li)=0.13	(4g) (0 0.169 0) OF(Mn)=0.93 OF(Li)=0.07	(4g) (0 0.169 0) OF(Mn)=0.955 OF(Li)=0.045
Oxygen ions layers	(4i) (0.241 0 0.218) OF (O) = 1	(4i) (0.229 0 0.221) OF (O) = 1	(4i) (0.233 0 0.219) OF (O) = 1	(4i) (0.236 0 0.219) OF (O) = 1	(4i) (0.232 0 0.216) OF (O) = 1
	(8j) (0.236 0.334 0.229) OF (O) = 1	(8j) (0.233 0.330 0.229) OF (O) = 1	(8j) (0.235 0.330 0.230) OF (O) = 1	(8j) (0.239 0.328 0.231) OF (O) = 1	(8j) (0.228 0.333 0.229) OF (O) = 1

Table S2. Refined cell parameters obtained by FAULTS.

Sample Name	**Cell Parameters**				**R-Factor**
	a	b	c	β	%
W1	4.942	8.552	5.029	109.19	11.3
W2E1	4.942	8.556	5.029	109.2	11
W1E1	4.944	8.561	5.023	109.2	8.1
W1E2	4.945	8.559	5.028	109.24	10.9
E1	4.945	8.558	5.029	109.24	11.1

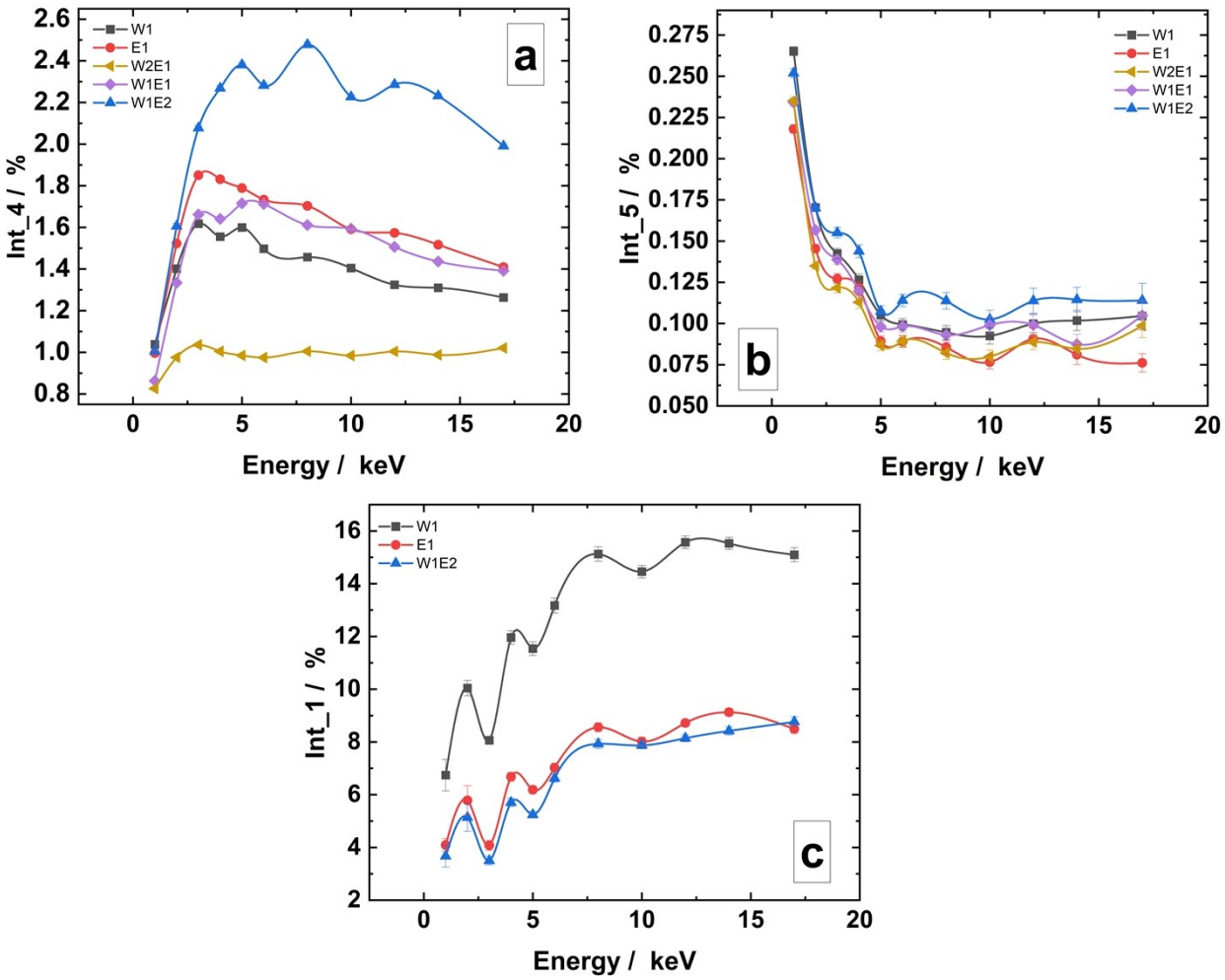

Figure S5. Intensity values of Tau4 (a), Tau5 (b) and Tau1 (c) lifetime components as function of energy for the different samples, from PAL spectroscopy.

Table S3. Fitting parameters of Ni 2p3/2 and Mn 2p3/2 XPS spectra.

	W1				W2E1				W1E1				W1E2				E1			
Mn $3p_{3/2}$	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Position	FWHM	Area/(RSF*T*MFP)	%At Conc
Mn 1 (IV)	642.41	1.50	6680.7	32.2	642.29	1.39	6484.4	32.9	642.35	1.55	7363.0	30.7	642.44	1.52	4928.3	28.7	642.26	1.44	6509.1	30.5
Mn 2 (IV)	643.19	1.63	3567.5	17.2	643.07	1.59	3462.7	17.6	643.13	1.56	3931.9	16.4	643.22	1.49	2631.7	15.4	643.04	1.44	3475.9	16.3
Mn3 (IV)	643.78	1.68	3313.6	16.0	643.66	1.53	3216.3	16.3	643.72	1.70	3652.1	15.3	643.81	1.67	2444.4	14.3	643.63	1.36	3228.5	15.1
Mn4 (IV)	644.48	1.70	1850.6	8.9	644.36	1.70	1796.2	9.1	644.42	1.70	2039.6	8.5	644.51	1.70	1365.1	8.0	644.33	1.70	1803.0	8.5
Mn5 (IV)	645.26	1.70	1115.7	5.4	645.14	1.70	1082.9	5.5	645.20	1.43	1229.6	5.1	645.29	1.42	823.0	4.8	645.11	1.51	1087.0	5.1
Mn6 (IV)	646.17	1.39	581.2	2.8	646.05	1.38	564.1	2.9	646.11	1.25	640.6	2.7	646.20	1.17	428.8	2.5	646.02	1.34	566.3	2.7
Mn7 (IV)	647.26	1.40	240.5	1.2	647.14	1.28	233.4	1.2	647.20	1.35	265.1	1.1	647.29	1.18	177.4	1.0	647.11	1.28	234.3	1.1
Tot Mn(IV)				**83.5**				**85.4**				**79.8**				**74.6**				**79.3**
Mn 1 (III)	640.55	1.57	854.9	4.1	640.30	1.43	716.2	3.6	640.54	1.70	1206.7	5.0	640.68	1.70	1085.6	6.3	640.75	1.61	1102.8	5.2
Mn 2 (III)	641.34	1.31	859.2	4.1	641.09	1.00	719.8	3.7	641.33	1.40	1212.8	5.1	641.47	1.37	1091.1	6.4	641.54	1.54	1108.4	5.2
Mn3 (III))	642.02	1.64	685.6	3.3	641.77	1.52	574.4	2.9	642.01	1.00	967.8	4.0	642.15	1.00	870.7	5.1	642.22	1.00	884.5	4.1
Mn4 (III)	642.78	1.70	531.0	2.6	642.53	1.70	444.8	2.3	642.77	1.70	749.5	3.1	642.91	1.70	674.3	3.9	642.98	1.61	685.0	3.2
Mn5 (III)	643.60	1.00	280.1	1.3	643.35	1.00	234.6	1.2	643.59	1.00	395.4	1.7	643.73	1.13	355.7	2.1	643.80	1.70	361.3	1.7
Mn6 (III)	644.44	1.70	150.4	0.7	644.19	1.70	126.0	0.6	644.43	1.09	212.2	0.9	644.57	1.00	190.9	1.1	644.64	1.00	194.0	0.9
Mn7 (III)	645.46	1.00	62.7	0.3	645.21	1.70	52.5	0.3	645.45	1.70	88.5	0.4	645.59	1.29	79.6	0.5	645.66	1.70	80.9	0.4
Tot Mn(III)				**16.5**				**14.6**				**20.2**				**25.4**				**20.7**

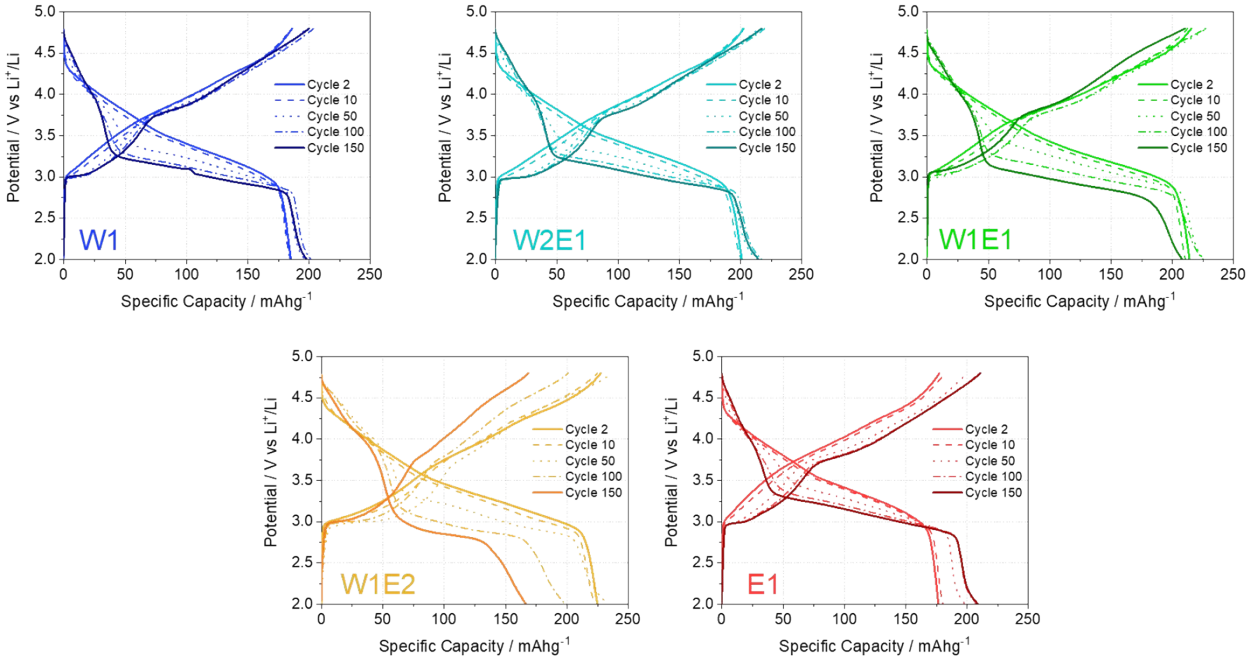

Figure S6. Potential profile of selected cycles obtained in half-cell configuration by galvanostatic cycling using a voltage range of 2-4.8V at C/10.

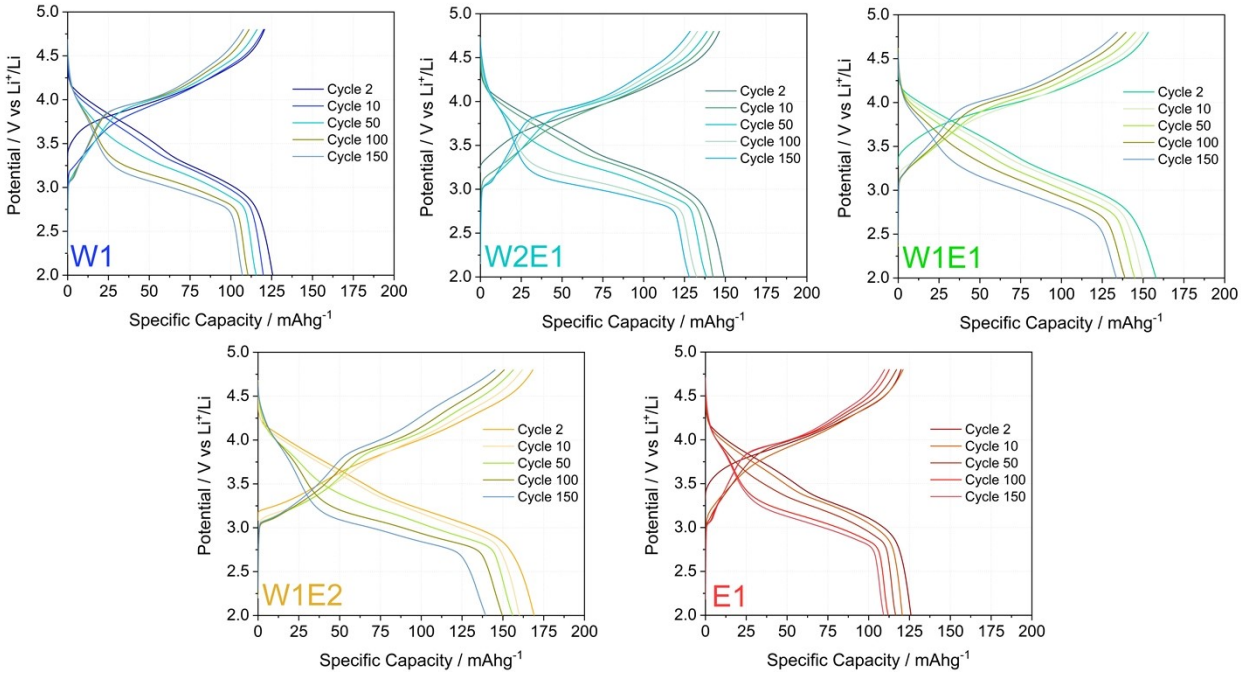

Figure S7. Potential profile of selected cycles obtained in half-cell configuration by galvanostatic cycling using a voltage range of 2-4.8V at 1C.

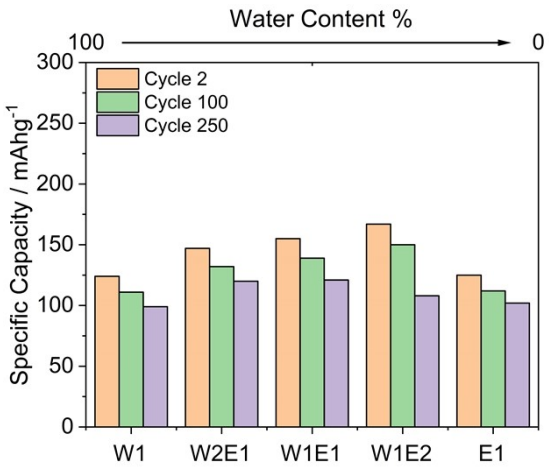

Figure S8. Summary of specific capacity obtained after 2, 100 and 250 cycle as function of water content in the reaction solvent obtained in half-cell configuration by galvanostatic cycling using a voltage range of 2-4.8V at 1C.

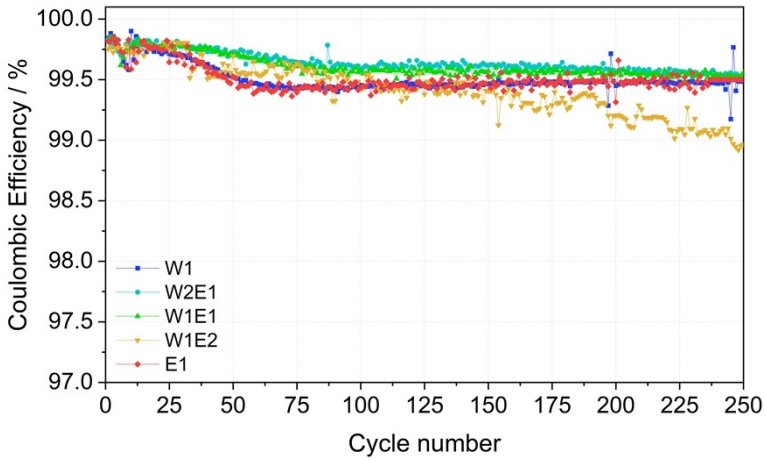

Figure S9. Coulombic Efficiency as function of cycle number cycles obtained for all the samples by galvanostatic cycling using a voltage range of 2-4.8V at 1C.

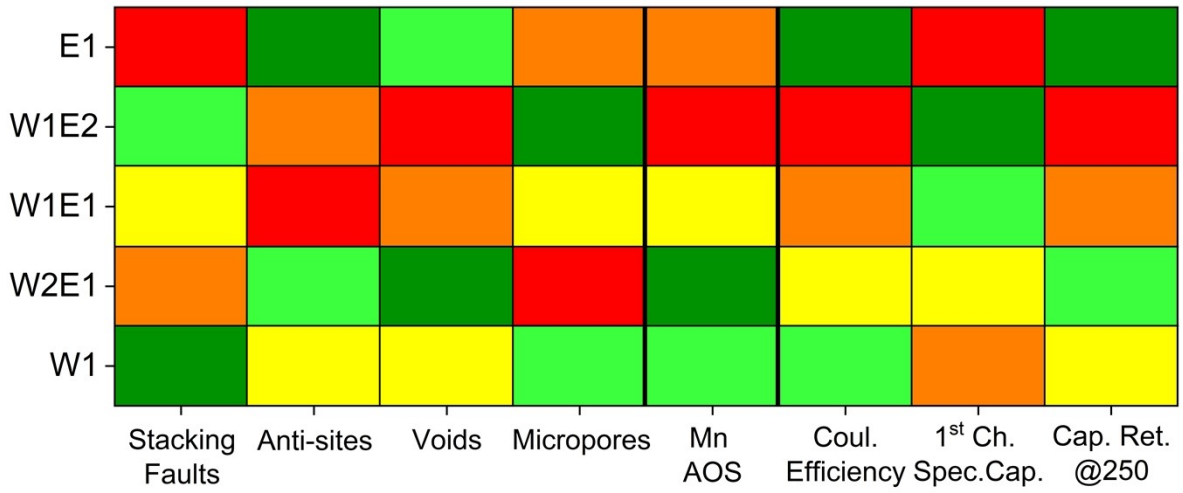

Figure S10. Correlation between defectivity and electrochemical behaviour.