

Supplementary Information

Effect of the nature of the electrolyte on the behaviour of supercapacitors based on transparent ZnMn₂O₄ thin films

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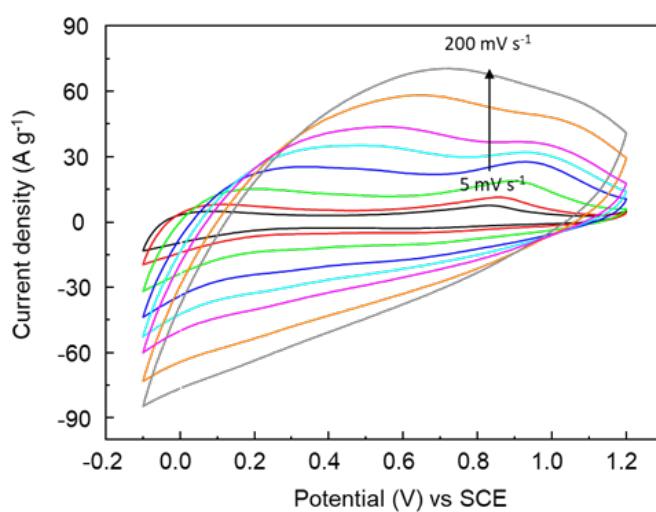
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1. Optical properties

Sample	Visible transmittance (from 380 to 770 nm) D65	Solar transmittance (from 295 to 2415 nm)	Colorimetric coordinates CIE 1931	Colorimetric coordinates CIELAB (1976, 2°, D65)
ITO	0.82	0.79	Y=81.81, x=0.31, y=0.32	L*= 92.49, a* = 1.03, b* = -3.01
ITO/ZnMn ₂ O ₄ (2 min)	0.72	0.71	Y=71.29, x=0.33, y=0.35	L*= 87.83, a* = -1.16, b* = 8.73
ITO/ZnMn ₂ O ₄ (5 min)	0.57	0.63	Y=56.6, x=0.35, y=0.36	L*= 79.95, a* = 0.71, b* = 16.62
ITO/ZnMn ₂ O ₄ (15 min)	0.30	0.48	Y=30.49, x=0.4, y=0.4	L*= 62.07, a* = 5.72, b* = 30.81

Table SI 1: Visible and solar transmittance values, and colorimetric coordinates

2. Three-electrode electrochemical cell characterization of ZnMn₂O₄ electrodes Figure SI 1:



Three-electrode cyclic voltammogram curves at different scan rates: 5, 10, 25, 50, 75, 100, 150 and 200 mV s⁻¹.

Deposition method	Electrode	Electrolyte	Specific capacitance ($F\ g^{-1}$)	Capacitance retention (%)	Energy density ($W\ h\ kg^{-1}$)	Power density ($W\ kg^{-1}$)	Reference
Pneumatique Spray deposition	ZnMn ₂ O ₄	1M Na ₂ SO ₄	752 (0.5A g ⁻¹) 693 (5 mV s ⁻¹)	70% after 3000 cycles	1-8	300-1000	This study
	ZnMn ₂ O ₄	2M KOH	155 (2 mV s ⁻¹)	*	*	*	[45]
Hydrothermal method	ZnMn ₂ O ₄	1M KCl	675 (5 mV s ⁻¹)	61.7 % after 1000 Cycles	*	*	[74]
	ZnMn ₂ O ₄	1M Na ₂ SO ₄	87 (1 mV s ⁻¹)	60 % after 1000 Cycles	*	*	[75]
	ZnMn ₂ O ₄	2 M KOH	54 (20 mV s ⁻¹)	*	*	*	[76]
	ZnMn ₂ O ₄	2 M KOH	776 (5 mV s ⁻¹)	91 % after 5000 cycles	*	*	[77]
Combustion method	Carbon-ZnMn ₂ O ₄	Na ₂ SO ₄	150 (2 mV s ⁻¹)	60 % after 10000 cycles	*	*	[2]
	ZnMn ₂ O ₄	2 M KOH	160 (3 mV s ⁻¹)	100% after 500 cycles	18	185	[70]
Ultrasonication	ZnMn ₂ O ₄ -Mn ₂ O ₃	2 M KOH	380 (0.5 A g ⁻¹)	92 % after 2000 cycles	*	*	[78]

* Non data available

Table SI 2: Values of specific capacitance obtained by different authors

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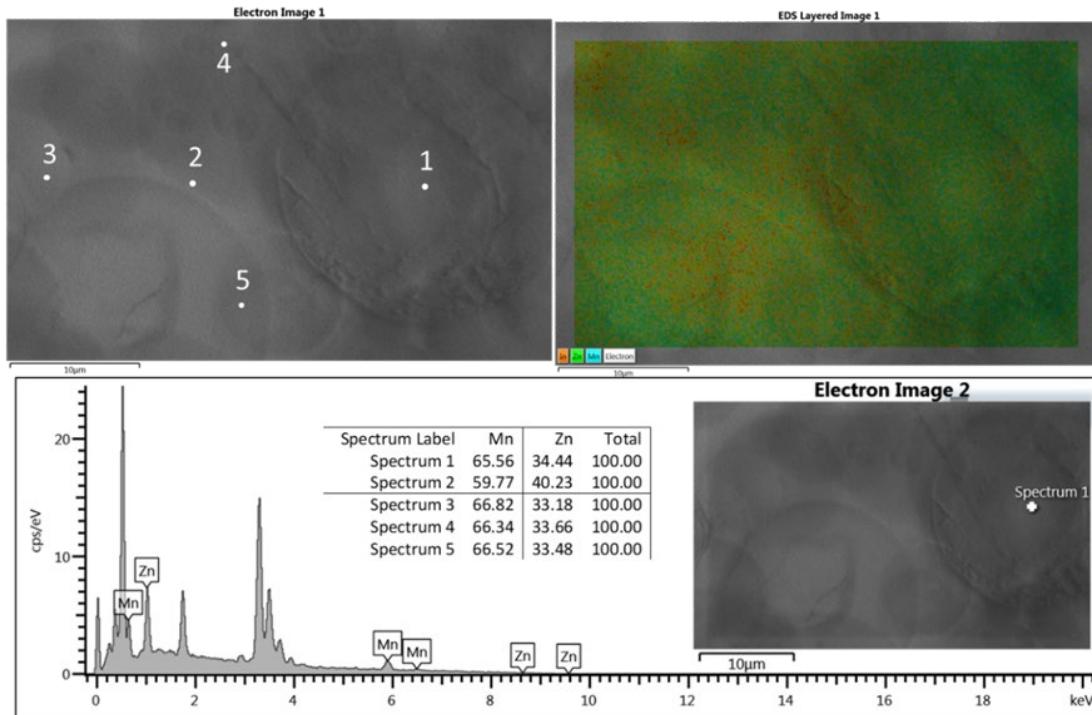


Figure SI 2: Example of EDS spectrum of the ZnMn₂O₄ electrode as obtained, and atomic percentages of Mn and Zn.

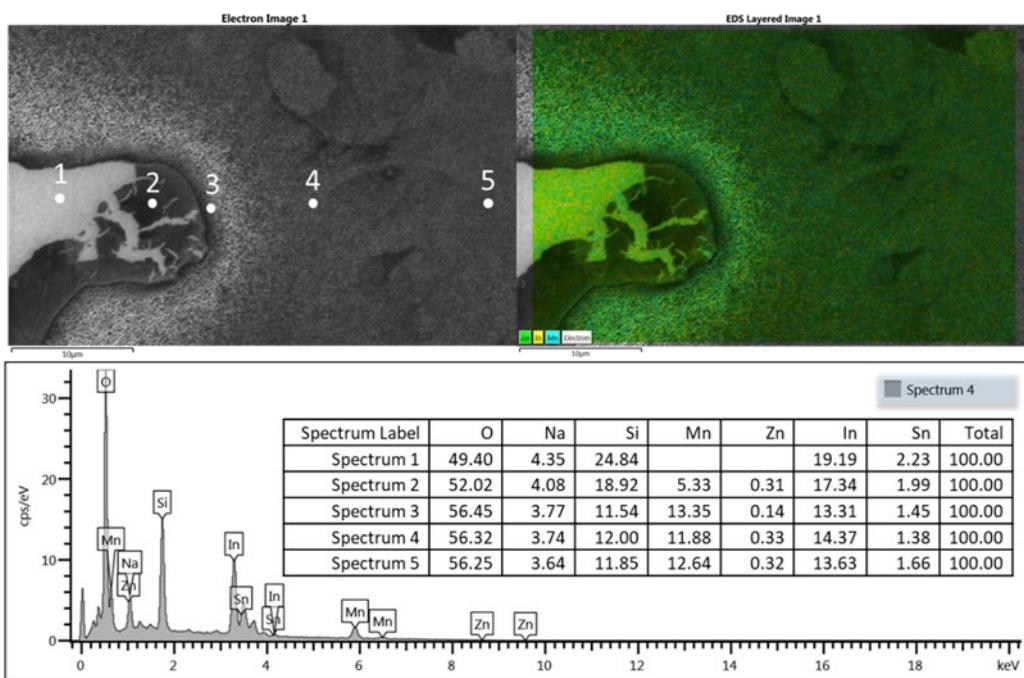


Figure SI 3: Example of EDS spectrum of the ZnMn₂O₄ electrode after 3000 CV cycles and local values of the atomic percentage of the different chemical elements.

3. SCC, 1 M Na₂SO₄ electrolyte

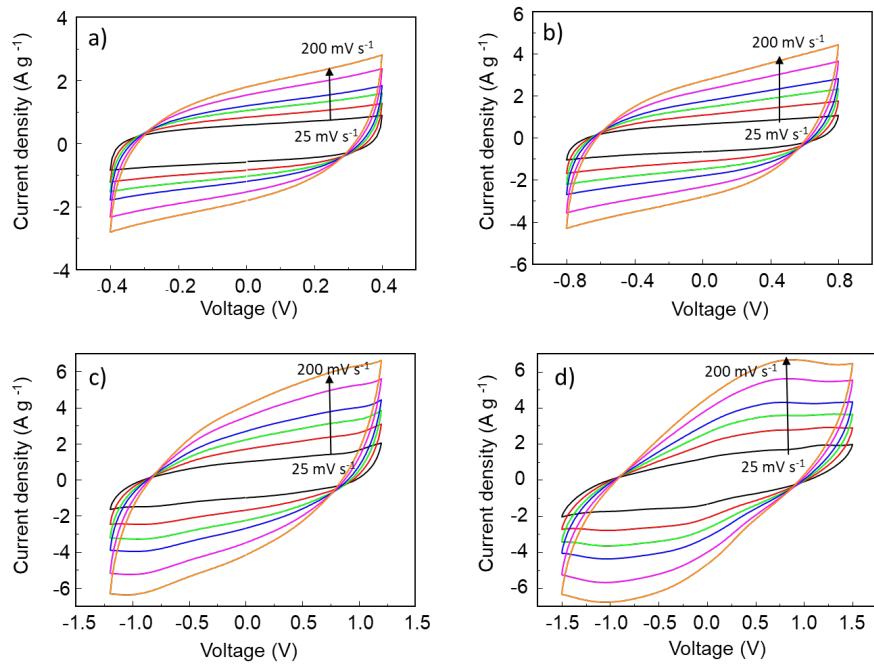


Figure SI 4: Cyclic voltammetry curves of SSC assembled with 1 M Na₂SO₄. (a) ± 0.4 V; (b) ± 0.8 V; (c) ± 1.2 V; d) ± 1.5 V with different scan rates: 25 mV s⁻¹, 50 mV s⁻¹, 75 mV s⁻¹, 100 mV s⁻¹, 150 mV s⁻¹ and 200 mV s⁻¹.

(a)					
Specific capacitance (Fg ⁻¹)	Scan rate (mVs ⁻¹)	Potential window (V)			
		± 0.4	± 0.8	± 1.2	± 1.5
1M Na ₂ SO ₄	25	21	23	33	39
	50	15	19	28	30
	75	12	17	24	26
	100	10	15	21	23
	150	9	13	18	20
	200	8	11	16	17

(b)					
Electrolyte	Current Density (A g ⁻¹)	Time discharge (s)	Specific Capacitance (F g ⁻¹)	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)
1M Na ₂ SO ₄	0.5	40	17	3.4	306
	1.0	8	7	1.4	630
	2.0	1	2	0.4	1440

Table SI 3. (a) Specific capacitance, energy and power density calculated from cyclic voltammetry; (b) GCD measurements of the SSC assembled with 1.0 M Na₂SO₄ electrolyte

4. SCC, PVP-Ionic Liquid electrolyte

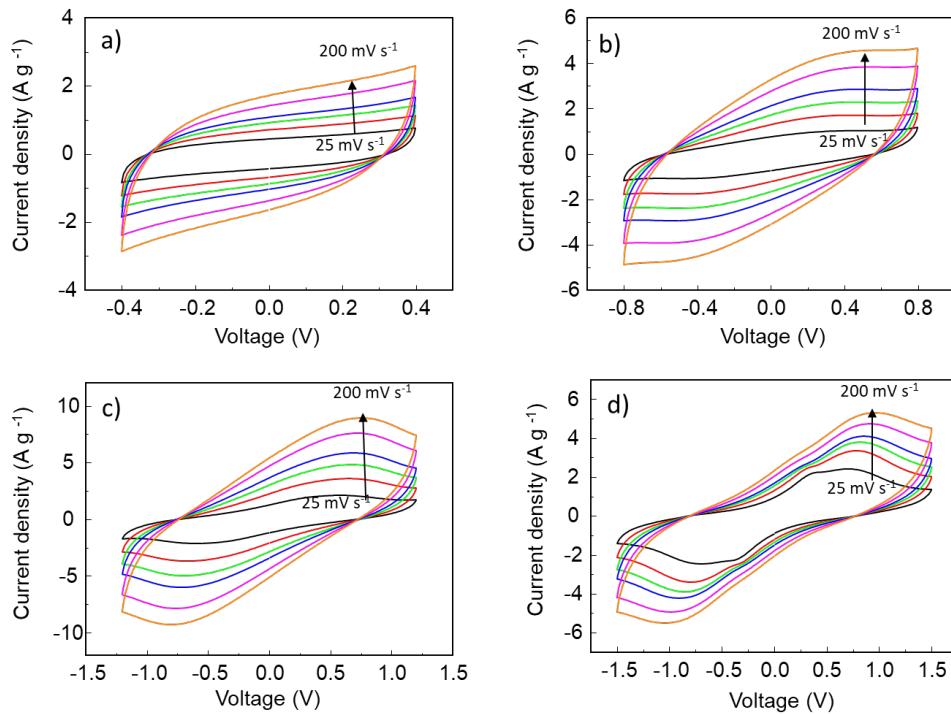


Figure SI 5. Cyclic voltammetry curves of SSC assembled with PVP-Ionic Liquid. (a) ± 0.4 V; (b) ± 0.8 V; (c) ± 1.2 V; (d) ± 1.5 V with different scan rates: 25 mV s^{-1} , 50 mV s^{-1} , 75 mV s^{-1} , 100 mV s^{-1} , 150 mV s^{-1} and 200 mV s^{-1} .

Specific capacitance (F g^{-1})	Scan rate (mVs^{-1})	Potential window (V)			
		± 0.4	± 0.8	± 1.2	± 1.5
PVP-Ionic Liquid	25	15	23	40	37
	50	11	20	35	29
	75	10	18	31	20
	100	9	16	28	16
	150	8	14	24	13
	200	7	13	21	11

Electrolyte	Current Density (A g^{-1})	Time discharge (s)	Specific Capacitance (F g^{-1})	Energy density (Wh kg^{-1})	Power density (W kg^{-1})
PVP-Ionic Liquid	0.5	35	15	3.0	309
	1.0	6	5	1.0	600
	2.0	2	3	0.6	1080

Table SI 4. (a) Specific capacitance, energy and power density calculated from cyclic voltammetry, (b) GCD measurements, of the SSC assembled with PVP-Ionic Liquid.

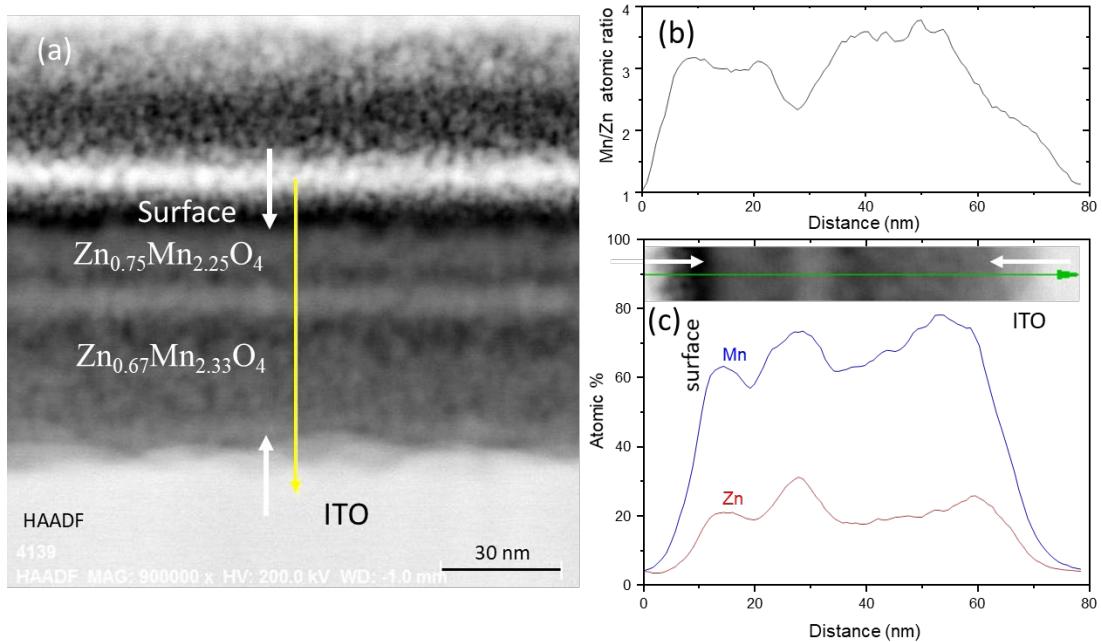
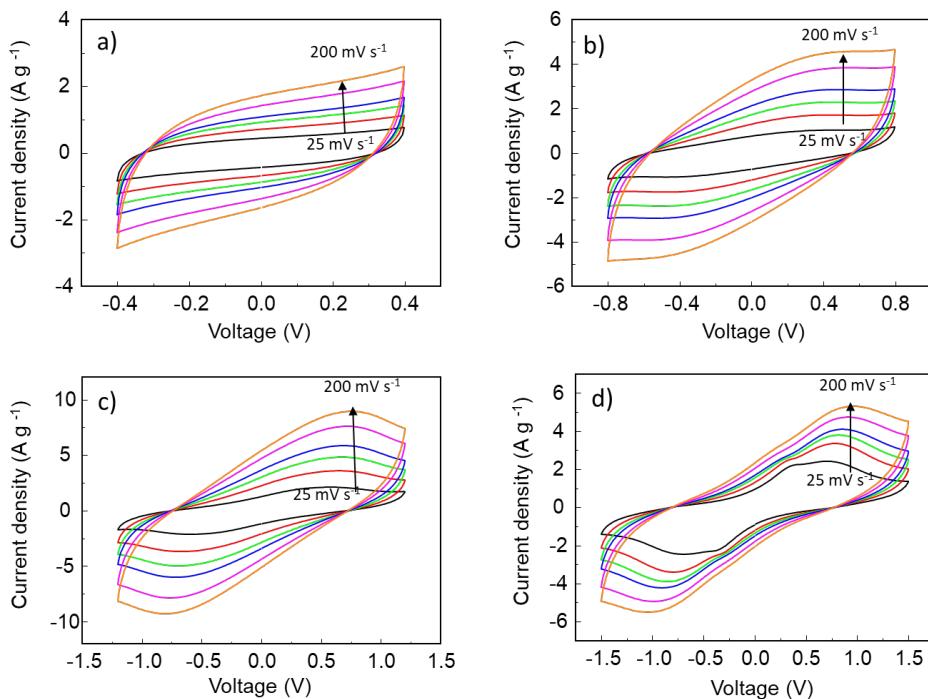


Figure SI 6: (a) HAADF image EDS of the cross-section of the SCC (PVP-Ionic Liquid) electrode after 300 CV cycles; (b) Mn/Zn atomic ratio and (c) atomic percentages of Mn and Zn, along the line marked on the HAADF image.

5. SCC, PVP-LiClO₄ electrolyte

Figure SI 7. Cyclic voltammetry curves of SSC assembled with PVP-Ionic Liquid. (a) ± 0.4 V; (b) ± 0.8 V; (c) ± 1.2 V; (d)



± 1.5 V with different scan rates: 25 mV s⁻¹, 50 mV s⁻¹, 75 mV s⁻¹, 100 mV s⁻¹, 150 mV s⁻¹ and 200 mV s⁻¹.

Specific capacitance ($F g^{-1}$)	Scan rate (mVs^{-1})	Potential window (V)			
		± 0.4	± 0.8	± 1.2	± 1.5
PVP-LiClO ₄	25	13	17	22	19
	50	12	16	19	16
	75	11	15	17	14
	100	10	14	15	12
	150	10	14	14	11
	200	9	13	13	10

(b)	Electrolyte	Current Density ($A g^{-1}$)	Time discharge (s)	Specific Capacitance ($F g^{-1}$)	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)
PVP-LiClO ₄	0.5	94	39	7.8	299	
	1.0	38	31	6.2	587	
	2.0	13	21	4.2	1163	

Table SI 5. (a) Specific capacitance, energy and power density calculated from cyclic voltammetry; (b) galvanostatic charge-discharge measurements of the SSC assembled with PVP-LiClO₄.

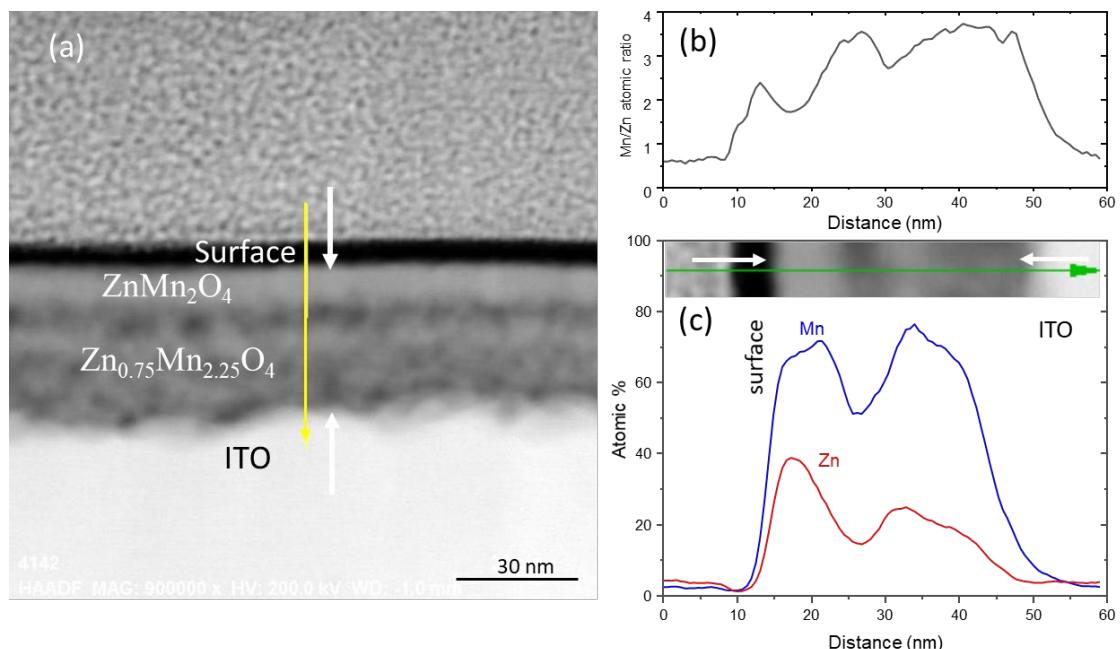


Figure S8: (a) HAADF image EDS of the cross-section of the SCC electrode (PVP-LiClO₄) after 300 CV cycles; (b) Mn/Zn atomic ratio and (c) atomic percentages of Mn and Zn, along the line marked on the HAADF image

6. SEM images of the SSCs electrodes after CV cycling

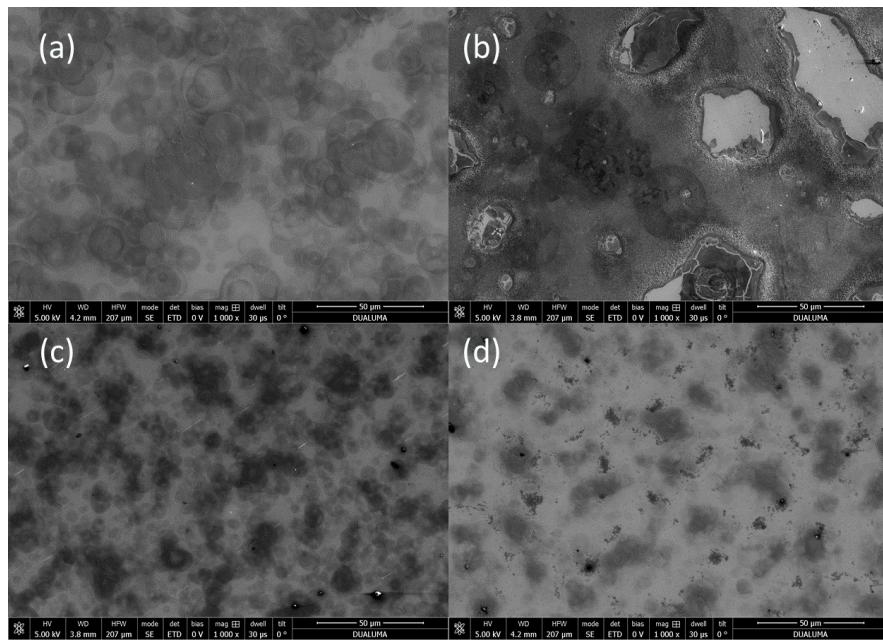


Figure SI 9: (a) SEM images of the surface of the electrode as obtained. SEM images of the surface of the SSC electrode after 300 CV cycles using as electrolyte: (b) 1.0 M Na_2SO_4 , (c) PVP-Ionic Liquid, (d) PVP- LiClO_4 .