Supporting Information

Electrochemical Performance and Structural Evolution of Spray Pyrolyzed Mn_3O_4 Thin Films in Different Aqueous Electrolytes: Effect of Anions and Cations

Pramitha Adoor.[1], Shreeganesh Subraya Hegde [2], Badekai Ramachandra Bhat [2], Sajan D. George[3], Raviprakash Yeenduguli [1*]

[1,*]*Semiconductor and Photovoltaics Lab, Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal-576104, Karnataka, India*

[2]*Catalysis and Materials Chemistry Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore-575025, Karnataka, India*

[3]*Centre for Applied Nanosciences, Department of Atomic and Molecular Physics, Manipal Academy of Higher Education, Manipal, 576104, Karnataka, India*

**Corresponding Author: Dr Raviprakash Y – raviprakash.y@manipal.edu*

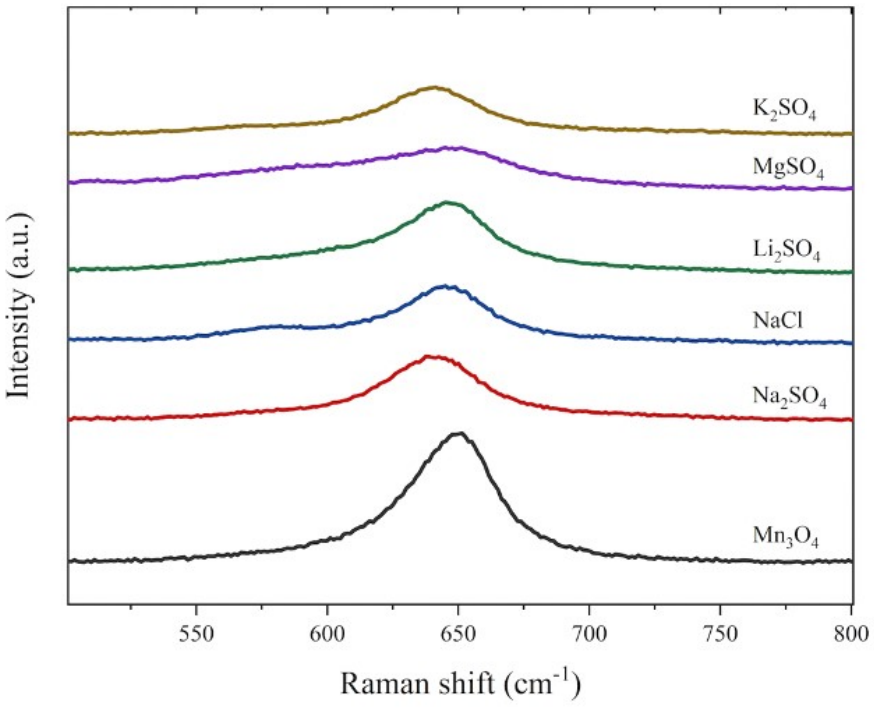


Figure S1: Comparison of Raman spectra before and after cycling in different electrolytes (in higher wavenumber region).

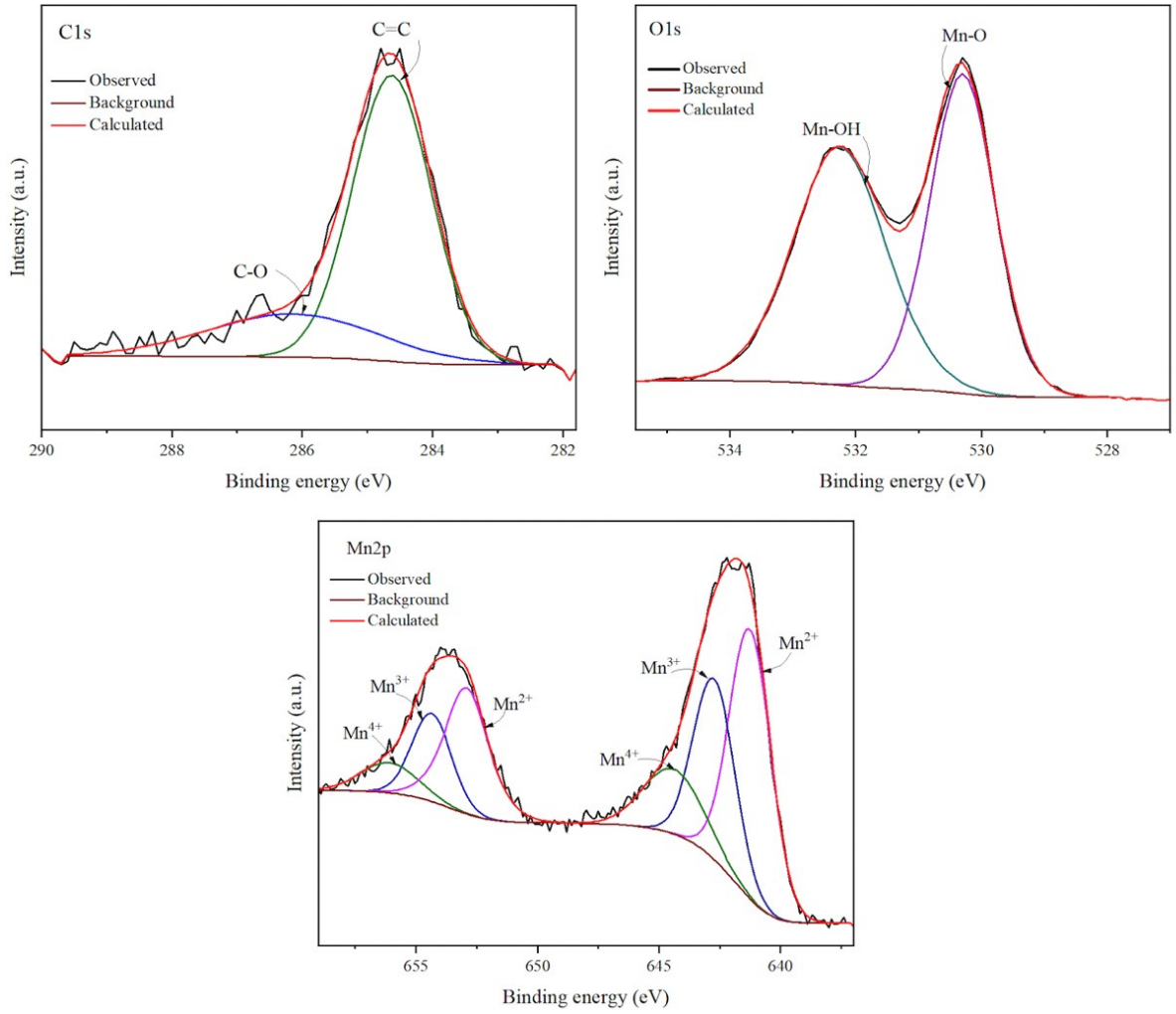


Figure S2: XPS core spectra of (a) C 1s, (b) O 1s and (c) Mn 2p of the electrode before cycling.

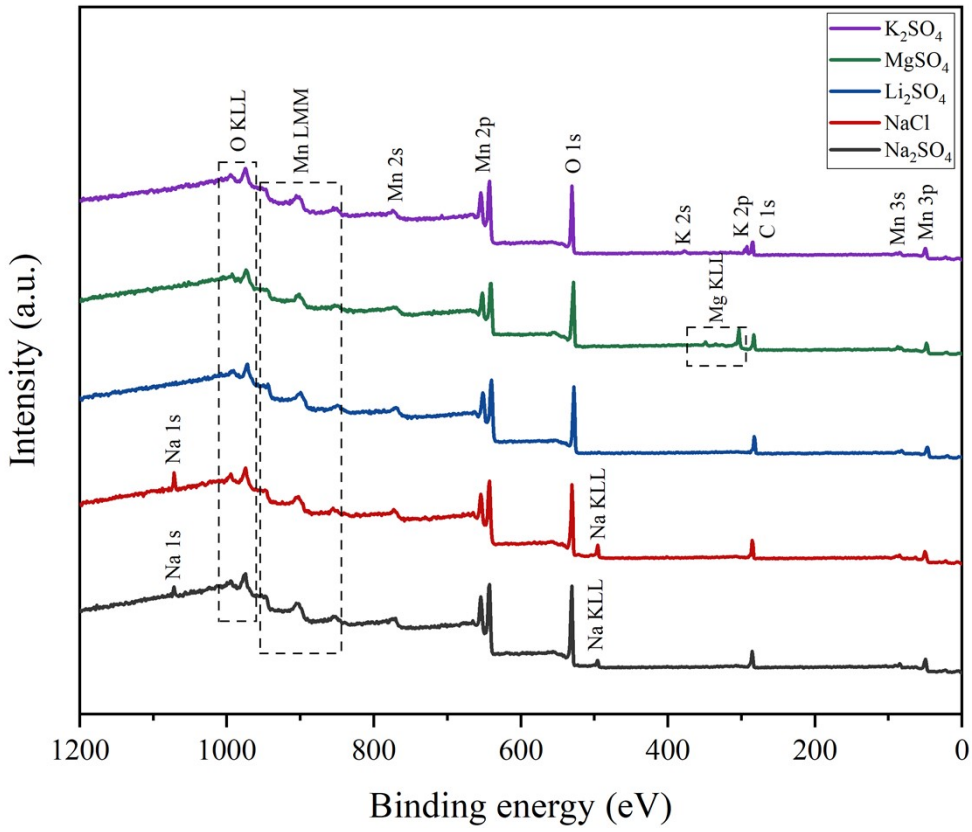


Figure S3: XPS Survey spectra of the electrodes after cycling in different electrolytes.

Table S1: Peak position, FWHM and area under the peaks obtained from XPS deconvolution.

Electrolyte used	Spin orbit split	Energy difference (eV)	Mn state	Peak position	FWHM	Area under the peak	Mn^{3+}/Mn^{2+}	Mn^{2+}/Mn^{4+}
Before cycling	Mn $2p_{3/2}$	11.75	Mn^{2+}	641.25	2.02	30050	0.66	2.88
			Mn^{3+}	642.73	2.00	19990		
			Mn^{4+}	644.40	2.90	10400		
	Mn $2p_{1/2}$		Mn^{2+}	652.92	2.10	15500		
			Mn^{3+}	654.35	1.90	9300		
			Mn^{4+}	656.09	2.75	4600		
Na_2SO_4	Mn $2p_{3/2}$	11.79	Mn^{2+}	640.84	1.58	11646	2.19	0.91
			Mn^{3+}	642.09	2.05	25570		
			Mn^{4+}	643.44	2.84	12834		
	Mn		Mn^{2+}	652.53	2.52	6827		

	$2p_{1/2}$		Mn^{3+}	653.70	2.17	13504		
			Mn^{4+}	655.25	2.90	6561		
NaCl	Mn $2p_{3/2}$	11.73	Mn^{2+}	640.70	2.33	9030	2.38	0.59
			Mn^{3+}	641.97	2.04	21580		
			Mn^{4+}	643.15	3.00	15890		
	Mn $2p_{1/2}$		Mn^{2+}	652.33	2.35	4958		
			Mn^{3+}	653.57	2.10	11531		
			Mn^{4+}	654.80	3.00	7904		
Li_2SO_4	Mn $2p_{3/2}$	11.69	Mn^{2+}	640.74	2.00	10850	2.28	0.89
			Mn^{3+}	641.99	2.05	24799		
			Mn^{4+}	643.65	2.76	12169		
	Mn $2p_{1/2}$		Mn^{2+}	652.31	2.15	5567		
			Mn^{3+}	653.56	2.10	12972		
			Mn^{4+}	655.32	3.00	6209		
$MgSO_4$	Mn $2p_{3/2}$	11.71	Mn^{2+}	641.10	2.04	6500	3.32	0.57
			Mn^{3+}	642.37	2.00	21624		
			Mn^{4+}	643.89	2.68	11000		
	Mn $2p_{1/2}$		Mn^{2+}	652.70	2.22	4500		
			Mn^{3+}	654.00	2.15	11420		
			Mn^{4+}	655.60	2.80	5000		
K_2SO_4	Mn $2p_{3/2}$	11.71	Mn^{2+}	640.94	1.85	9500	2.49	0.75
			Mn^{3+}	642.20	2.04	23675		
			Mn^{4+}	643.52	2.75	12560		
	Mn $2p_{1/2}$		Mn^{2+}	652.60	2.20	5390		
			Mn^{3+}	653.80	2.14	11891		
			Mn^{4+}	655.17	2.65	6150		

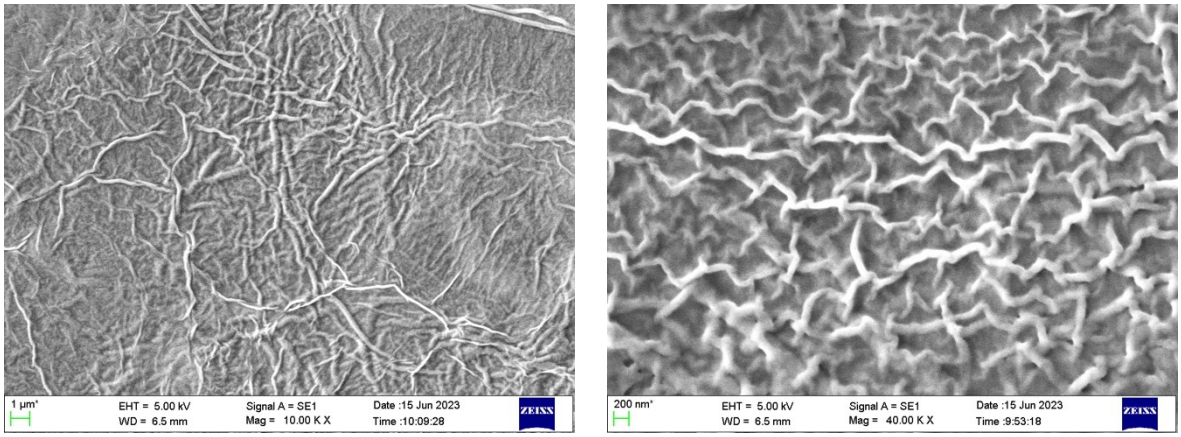
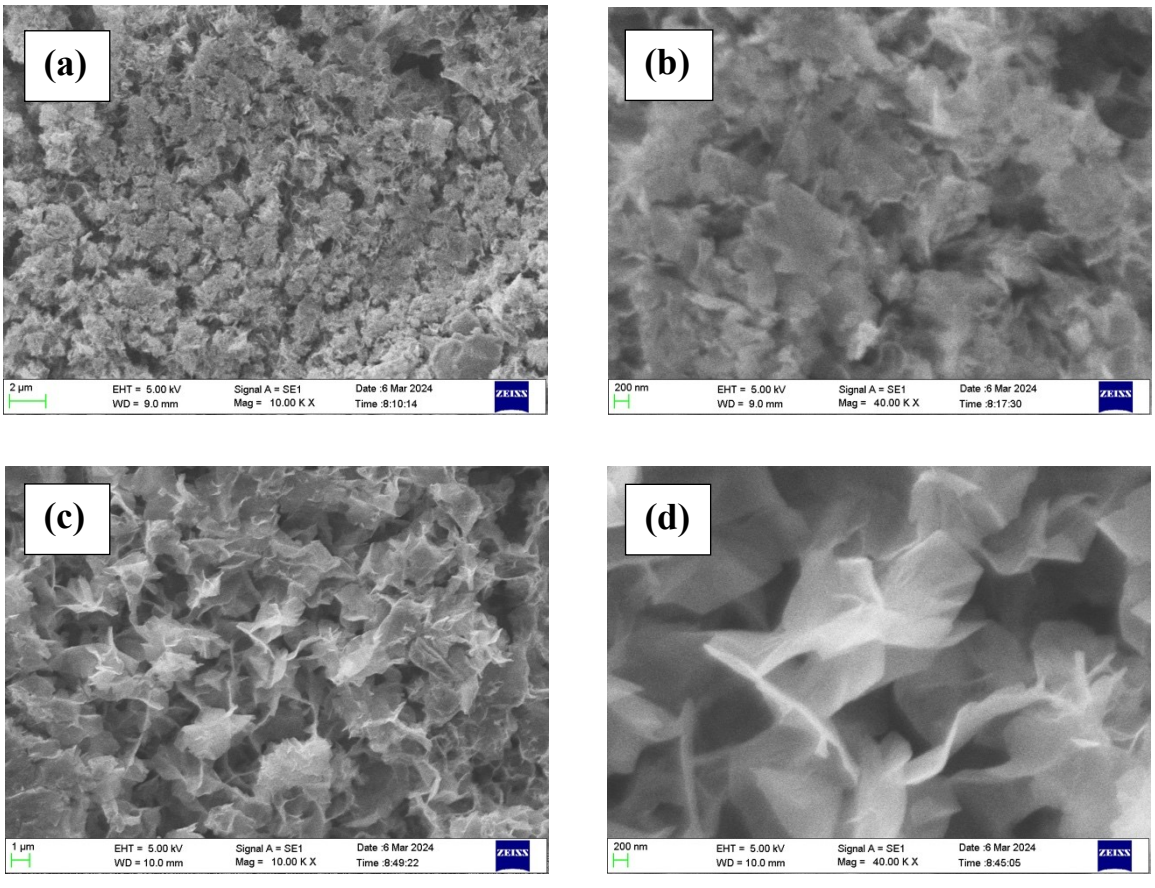


Figure S4: Different magnification SEM images of Mn_3O_4 thin film electrode before cycling



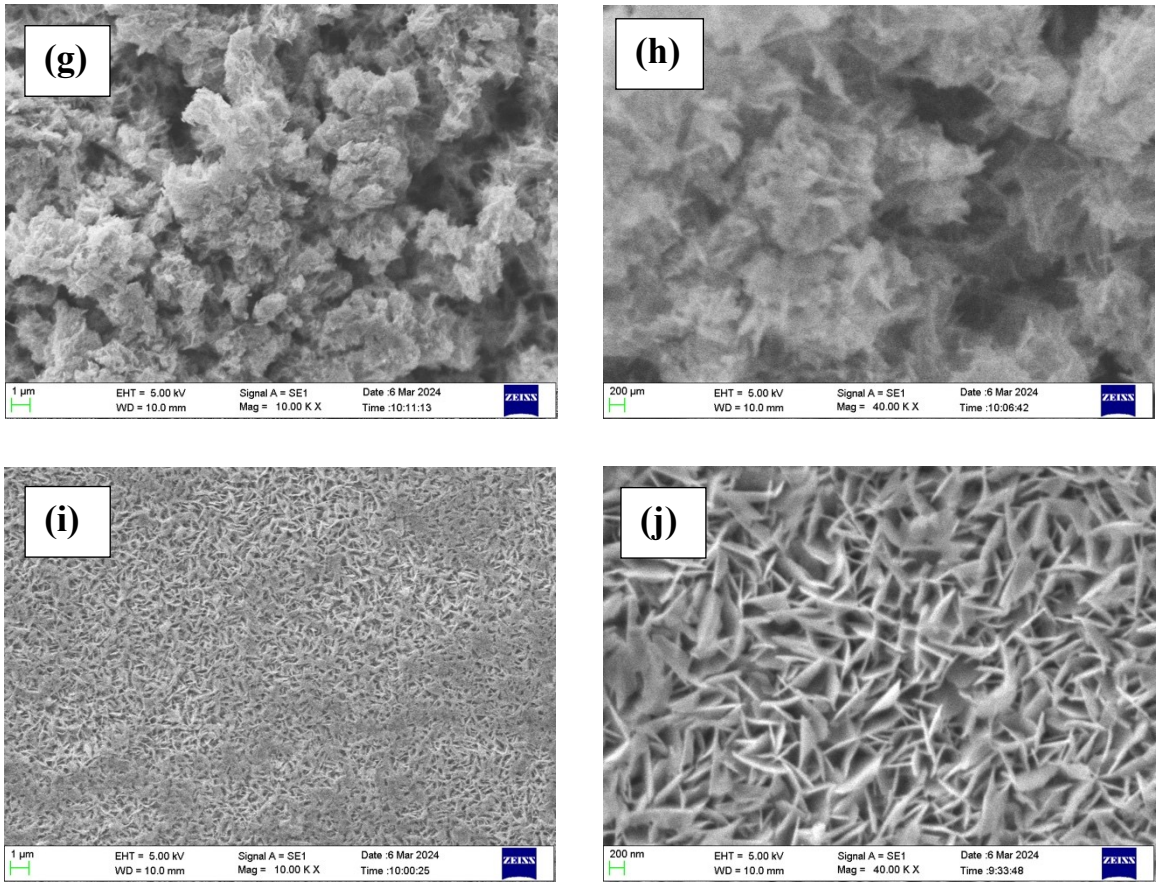


Figure S5: Different magnification SEM images of Mn_3O_4 thin film electrode after processed in (a) & (b) Na_2SO_4, (c) & (d) NaCl, (e) & (f) Li_2SO_4, (g) & (h) K_2SO_4, and (i) & (j) $MgSO_4$ for 500 CV cycles at 50 mV/s.

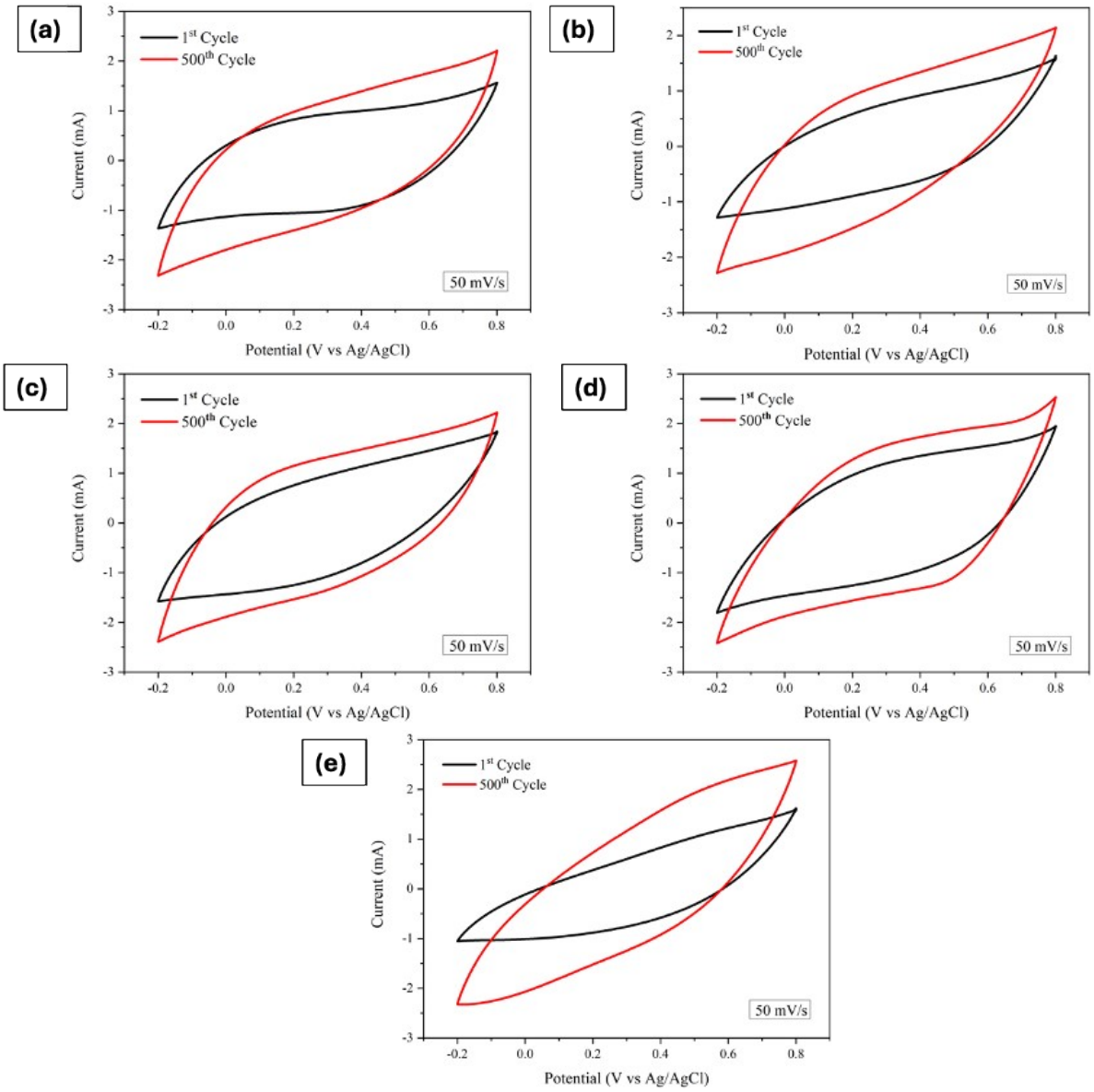


Figure S6: Comparison of 1st and 500th CV cycles of the electrodes processed in (a) Na_2SO_4, (b) NaCl, (c) Li_2SO_4, (d) K_2SO_4 and (e) $MgSO_4$.