Supporting information

Lithium-ion Coupled Electron Transfer Rates in Superconcentrated Electrolytes: Exploring the Bottlenecks for Fast Charge Transfer Rates with $LiMn_2O_4$ Cathode Materials

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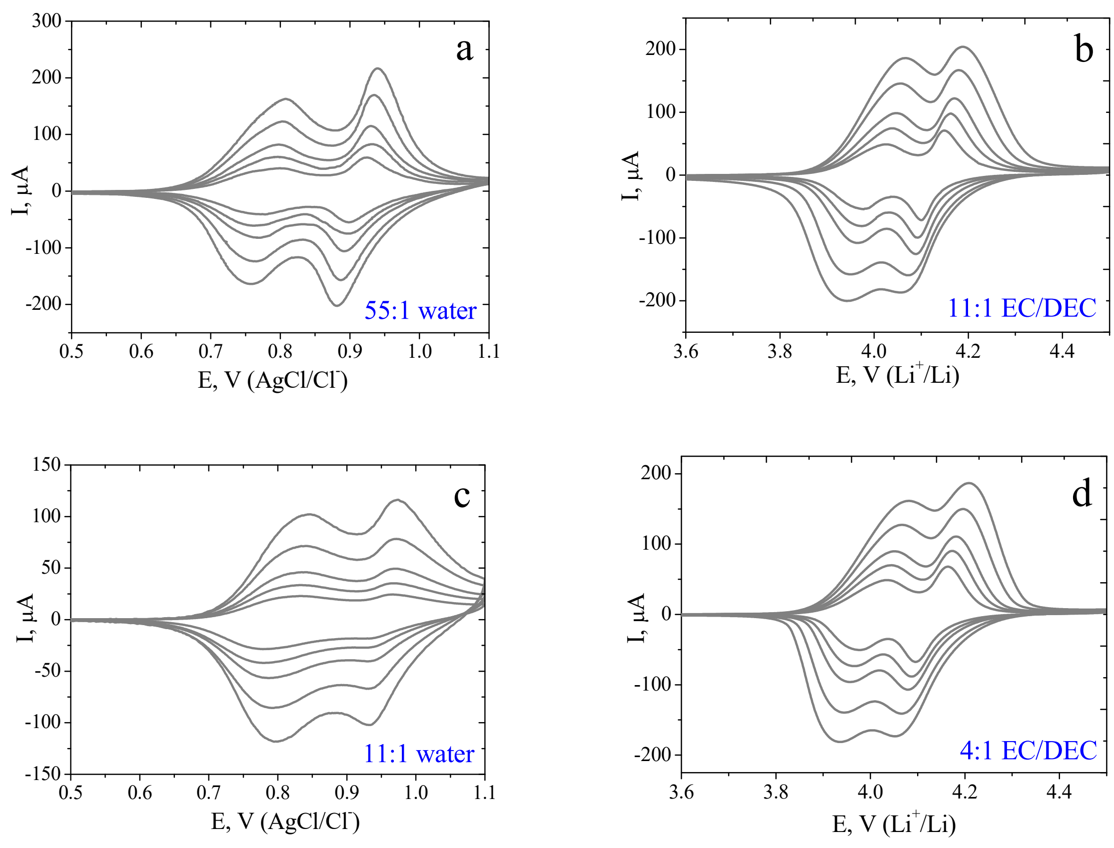

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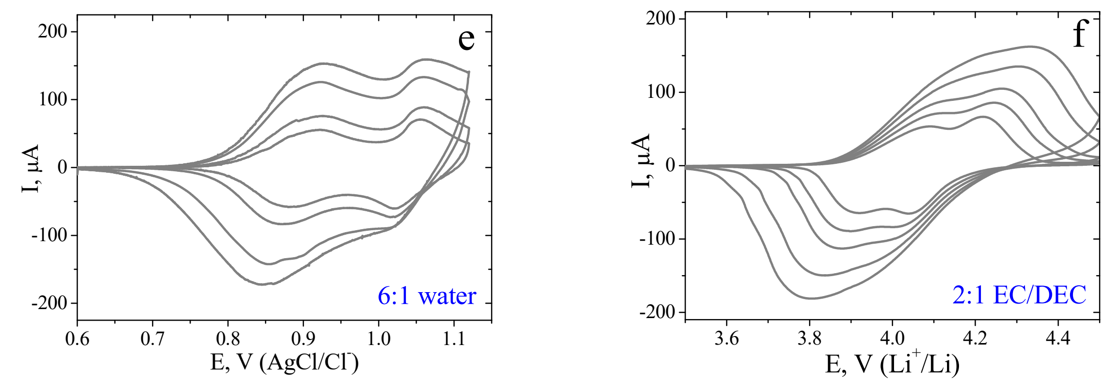

Figure S1. CVs of $LiMn_2O_4$ electrodes measured at potential scan rates: 50, 75, 100, 150, 200 $\mu V \cdot s^{-1}$ in 55:1 (a), 11:1 (c) and 6:1 (e) aqueous concentrated solutions and in 11:1 (b), 4:1 (d) and 2:1 (f) carbonate concentrated solutions.

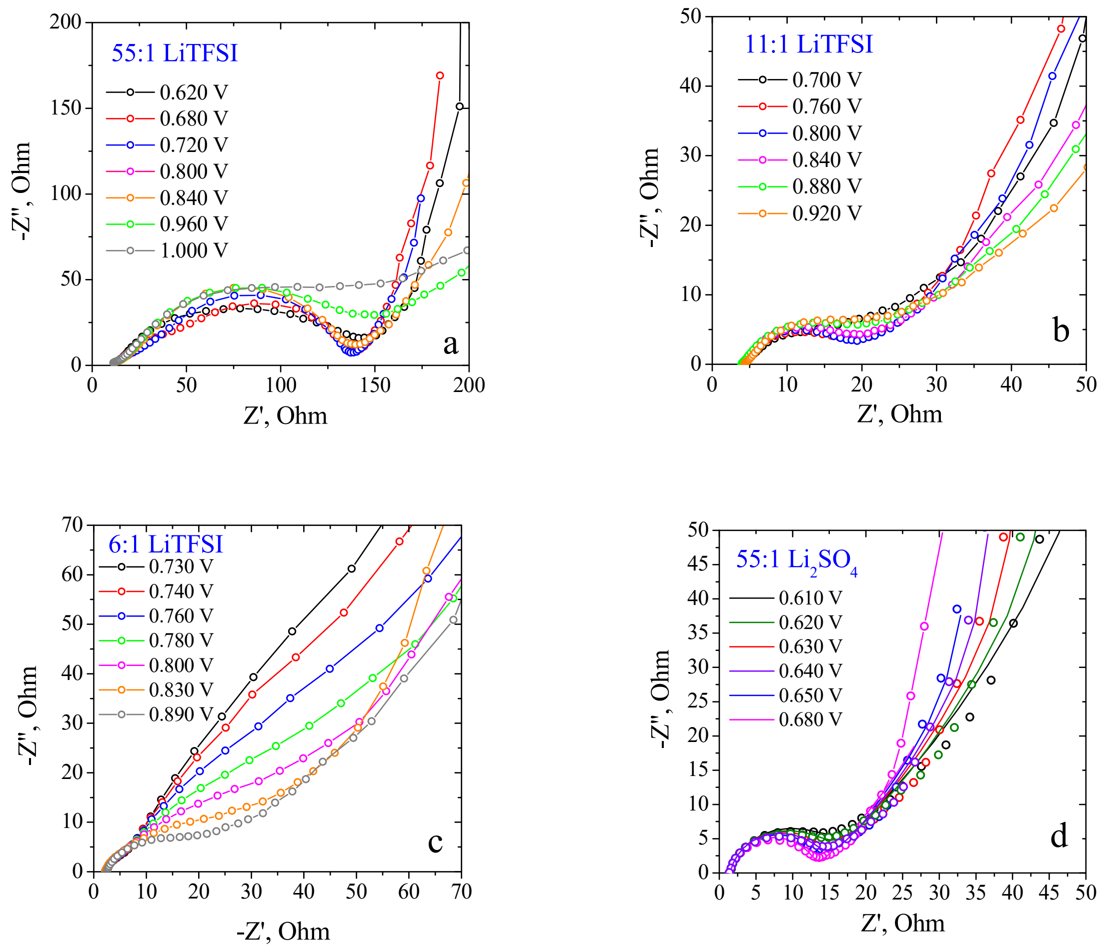

Figure S2. Nyquist plots for $LiMn_2O_4$ electrodes in aqueous LiTFSI solutions at selected potentials. The coulometric active material mass values for 55:1 LiTFSI, 11:1 LiTFSI, 6:1 LiTFSI and 55:1 Li_2SO_4 solutions are 0.27, 0.38, 0.56 and 0.39 mg, respectively.

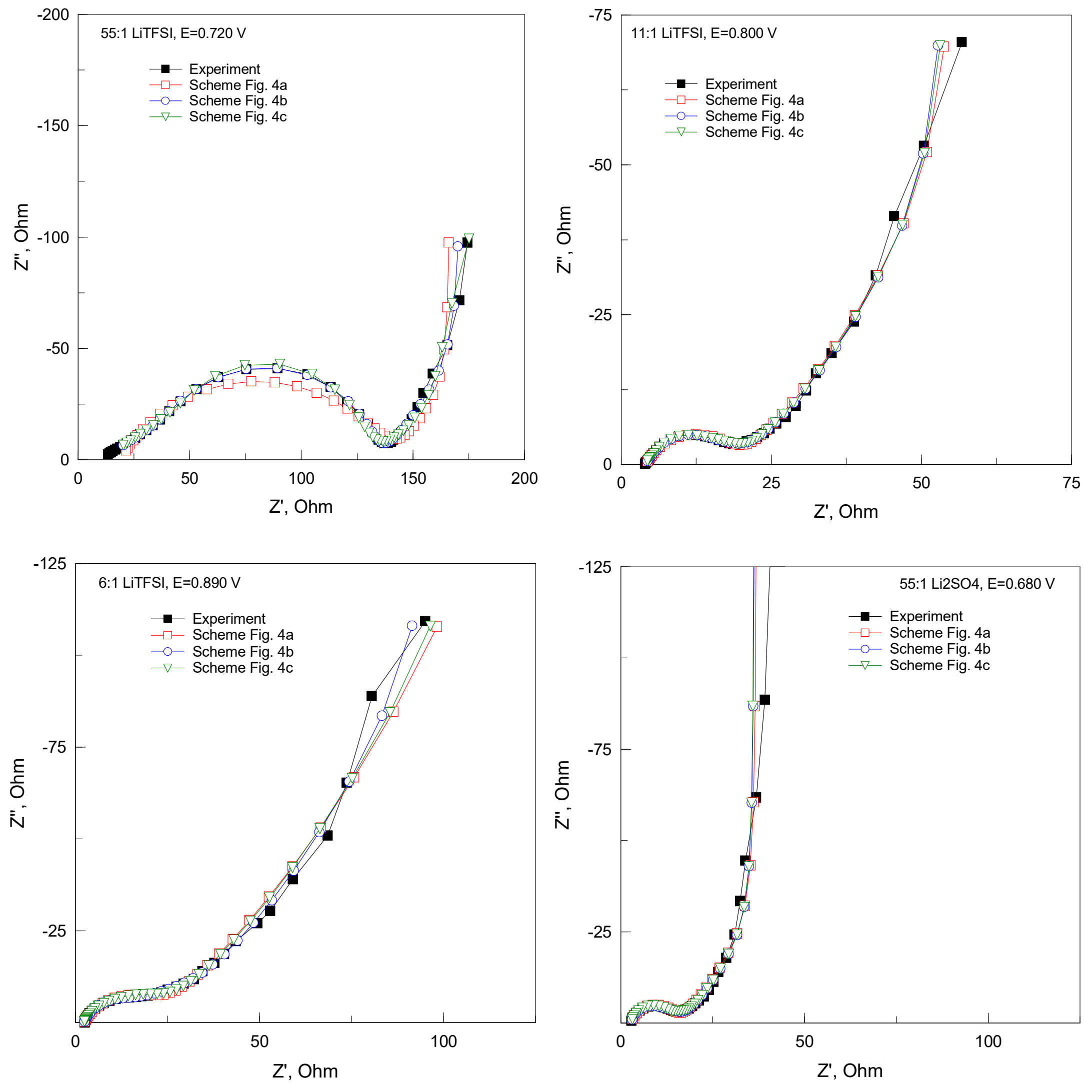

Figure S3. Fits of the experimental impedance spectra in aqueous LiTFSI solutions to the equivalent circuits in Figure 4.

Table S1. Parameters evaluated from the fitting of impedance spectra in aqueous LiTFSI solutions.

	Scheme	R_{sol}, Ohm	C_{dl}, F	φ_{dl}	R_{SEI}, Ohm	C_{SEI}, F	φ_{SEI}	$W_{sh}R$, Ohm	$W_{sh}C$, F	R_{ct}, Ohm	WR, Ohm	WC, F
55:1 LiTFSI	Fig. 4a	17.84±0.60	$1.81 \pm 0.19 \cdot 10^{-4}$	0.65±0.02						123.12±2.37	129±25	0.34±0.02
	Fig. 4b	11.63±0.66	$3.75 \pm 1.22 \cdot 10^{-4}$	0.50±0.04	85.98±4.63	$7.50 \pm 0.26 \cdot 10^{-5}$E	0.90±0.02			36.85±5.70	190±5	0.35±0.01
	Fig. 4c	7.97±0.73	$4.98 \pm 0.42 \cdot 10^{-3}$	0.27±0.01				91.30±1.11	$9.37 \pm 0.14 \cdot 10^{-5}$	48.13±3.01	142±11	0.24±0.01
11:1 LiTFSI	Fig. 4a	4.09±0.04	$9.07 \pm 0.45 \cdot 10^{-4}$	0.70±0.01						15.67±0.15	189±6	0.52±0.01
	Fig. 4b	3.86±0.06	$1.88 \pm 0.11 \cdot 10^{-2}$	0.42±0.01	9.04±0.38	$5.42 \pm 0.40 \cdot 10^{-4}$	0.84±0.02			12.13±0.63	158±4	0.27±0.01
	Fig. 4c	3.88±0.03	$2.59 \pm 0.39 \cdot 10^{-3}$	0.67±0.02				5.52±0.66	$5.28 \pm 0.62 \cdot 10^{-4}$	11.12±0.57	183±4	0.50±0.01
6:1 LiTFSI	Fig. 4a	2.33±0.04	$1.81 \pm 0.12 \cdot 10^{-3}$	0.69±0.01						22.09±0.49	545±64	0.43±0.04
	Fig. 4b	2.44±0.02	$9.21 \pm 0.14 \cdot 10^{-3}$	0.72±0.17	12.78±3.85	$1.22 \pm 0.07 \cdot 10^{-3}$	0.77±0.03			17.08±6.59	413±19	0.33±0.04
	Fig. 4c	2.26±0.04	$2.26 \pm 0.25 \cdot 10^{-3}$	0.72±0.04				2.84±1.20	$1.51 \pm 0.63 \cdot 10^{-3}$	20.07±1.43	507±52	0.41±0.03
55:1 Li2SO4	Fig. 4a	2.68±0.10	$2.58 \pm 0.33 \cdot 10^{-4}$	0.81±0.02						12.77±0.26	108±5	0.12±0.01
	Fig. 4b	2.93±0.12	$9.29 \pm 4.62 \cdot 10^{-4}$	0.96±0.12	5.57±5.42	$2.43 \pm 2.20 \cdot 10^{-3}$	0.76±0.21			7.25±5.13	103±54	0.12±0.01
	Fig. 4c	2.58±0.25	$2.83 \pm 0.94 \cdot 10^{-4}$	0.83±0.07				1.18±1.18	$6.18 \pm 6.18 \cdot 10^{-4}$	11.70±3.41	108±5	0.12±0.01

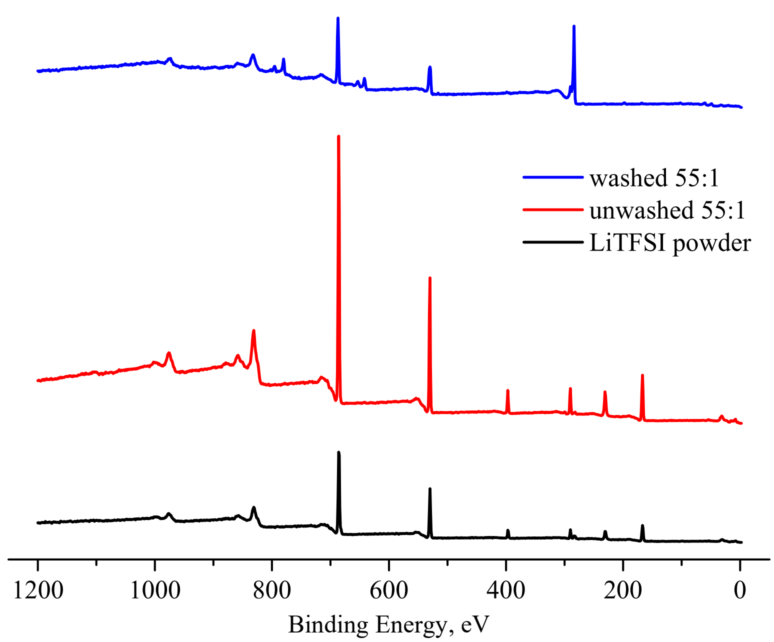

Figure S4. The unwashed samples demonstrate the salt spectrum.

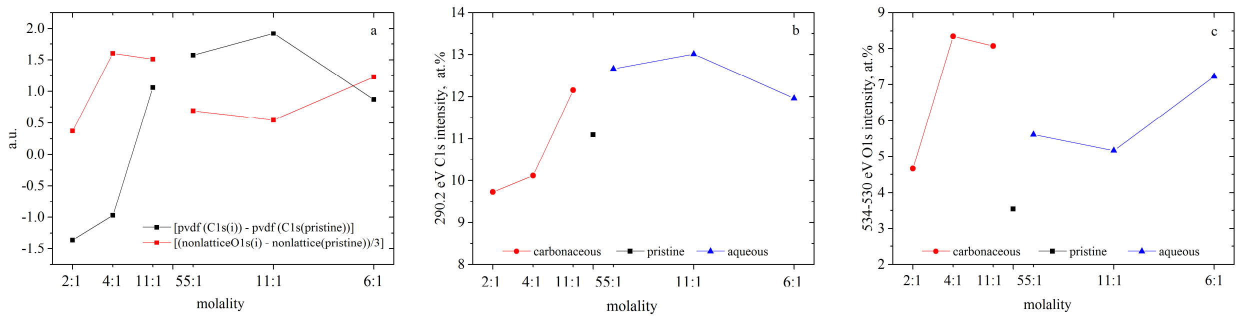

Figure S5. (a) The difference between non-lattice oxygen components in O1s spectrum and components of C 1s spectra at 290.2 eV corresponding to both PVDF and $–CO_3^{2-}$ (b) Atomic fraction of the C 1s peak at 290.2 eV for pristine electrode and electrodes cycled in carbonate (left) and aqueous (right) solutions (c) Atomic fraction of non-lattice oxygen for pristine electrode and electrodes cycled in carbonate (left) and aqueous (right) solutions.

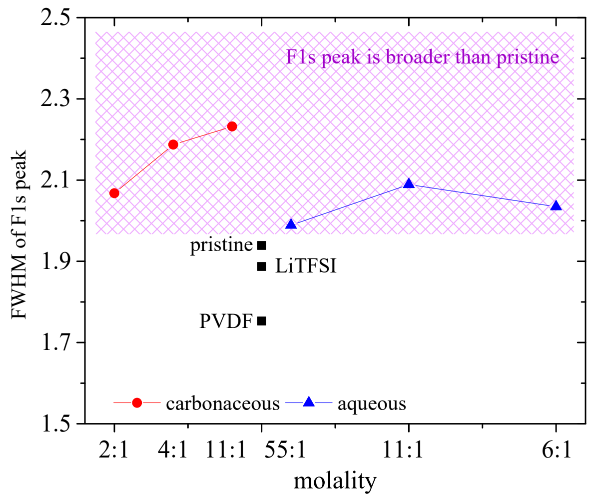

Figure S6. The width of the F 1s peak of pristine electrode and cycled electrodes in carbonate (left) and aqueous (right) solutions.

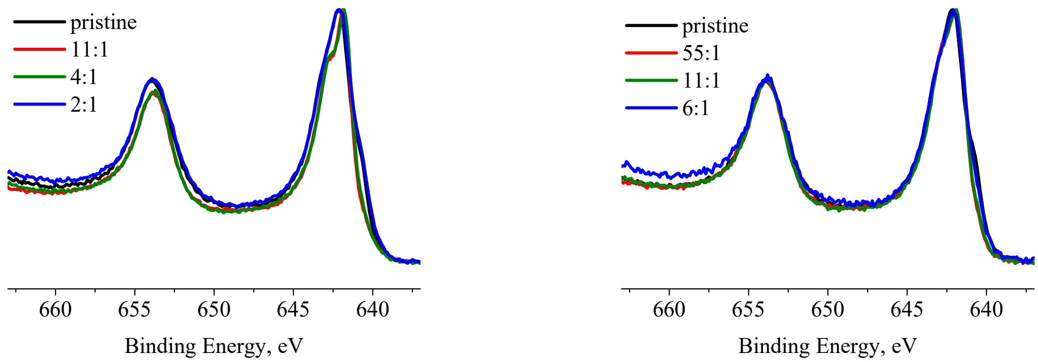

Figure S7. XPS spectra of Mn 2p peaks of pristine electrode and electrodes cycled in carbonate (left) and aqueous (right) solutions.

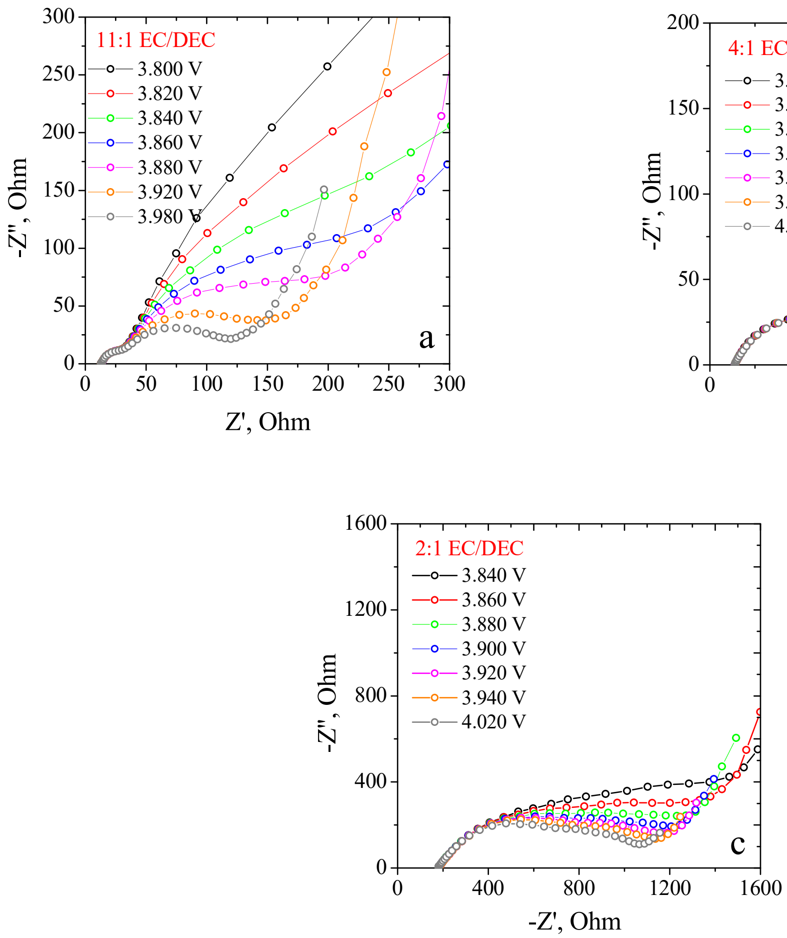

Figure S8. Nyquist plots for $LiMn_2O_4$ electrodes in EC/DEC LiTFSI solutions at selected potentials. The coulometric active material mass values for 11:1, 4:1 and 2:1 solutions are 0.18, 0.36 and 0.39 mg, respectively.

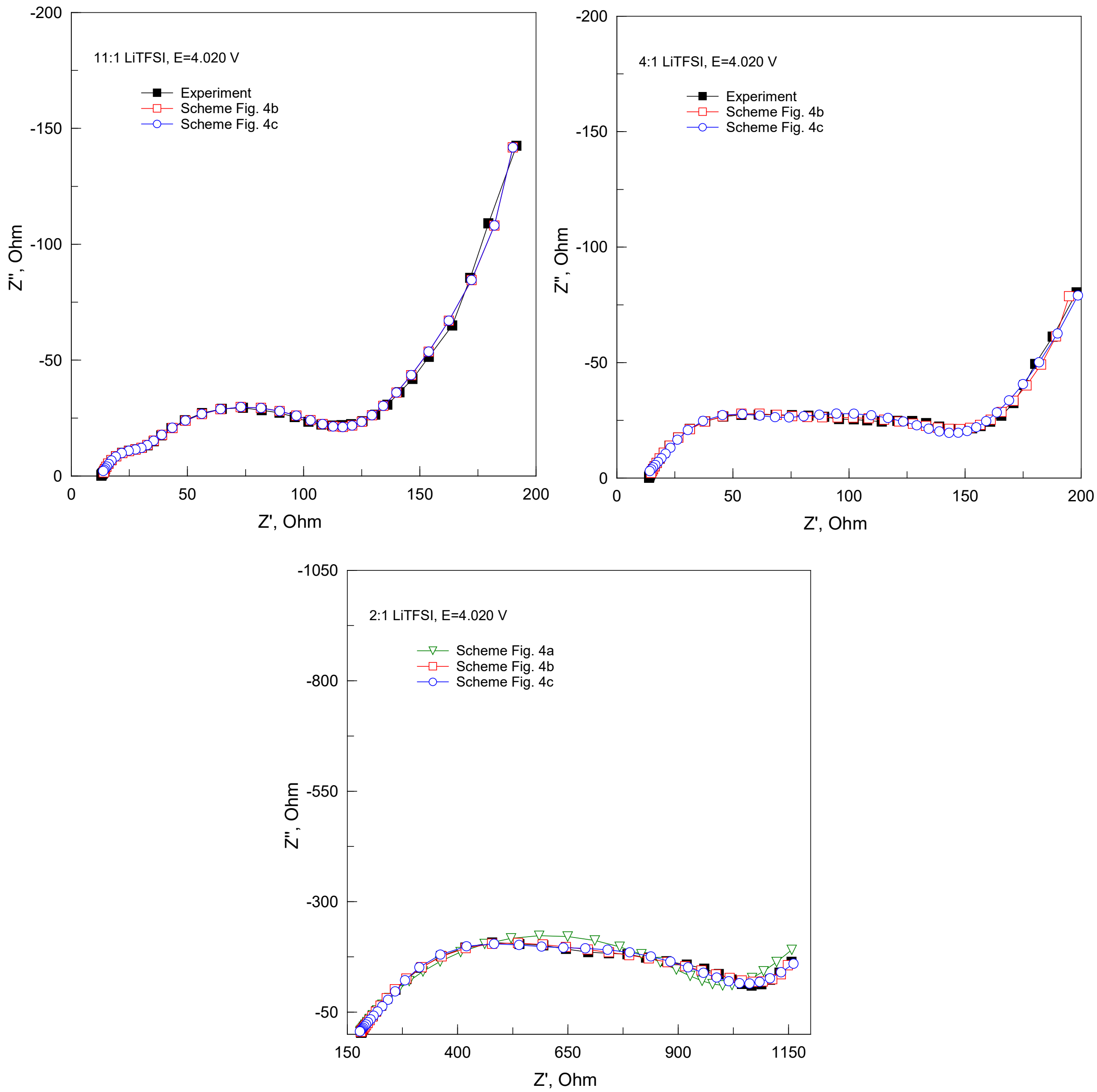

Figure S9. Fits of the experimental impedance spectra in carbonate LiTFSI solutions to the equivalent circuits in Figure 4.

Table S2. Parameters evaluated from the fitting of impedance spectra in carbonate LiTFSI solutions.

	Scheme	R_{sol}, Ohm	C_{dl}, F	φ_{dl}	R_{SEI}, Ohm	C_{SEI}, F	φ_{SEI}	$W_{sh}R$, Ohm	$W_{sh}C$, F	R_{ct}, Ohm	WR, Ohm	WC, F
11:1 LiTFSI	Fig. 4b	13.60±0.06	$8.05\pm0.17\cdot10^{-4}$	0.72±0.01	14.01±0.56	$5.25\pm0.52\cdot10^{-5}$	0.93±0.01			87.90±0.96	439±11	0.26±0.01
	Fig. 4c	12.00±0.07	$7.94\pm0.21\cdot10^{-4}$	0.72±0.01				14.80±0.42	$7.41\pm0.17\cdot10^{-5}$	88.65±0.94	441±14	0.26±0.01
4:1 LiTFSI	Fig. 4b	13.48±0.13	$2.11\pm0.12\cdot10^{-3}$	0.55±0.01	45.40±3.20	$1.16\pm0.07\cdot10^{-4}$	0.84±0.02			98.12±3.74	267±12	0.48±0.01
	Fig. 4c	11.43±0.17	$1.35\pm0.11\cdot10^{-3}$	0.63±0.03				41.86±3.45	$1.01\pm0.08\cdot10^{-4}$	94.57±4.96	385±97	0.59±0.11
2:1 LiTFSI	Fig. 4a	175.9±1.4	$2.16\pm0.07\cdot10^{-4}$	0.62±0.01						825.96±10.52	$10^{13}\pm10^{13}$	$10^{9}\pm10^{9}$
	Fig. 4b	176.2±0.5	$6.96\pm0.54\cdot10^{-4}$	0.51±0.01	245.2±19.5	$1.40\pm0.05\cdot10^{-4}$	0.87±0.02			723.27±14.90	389±78	0.30±0.03
	Fig. 4c	173.1±0.6	$5.99\pm0.37\cdot10^{-4}$	0.63±0.01				264.0±14.8	$1.64\pm0.09\cdot10^{-4}$	624.01±18.40	6942±6942	2.09±2.09

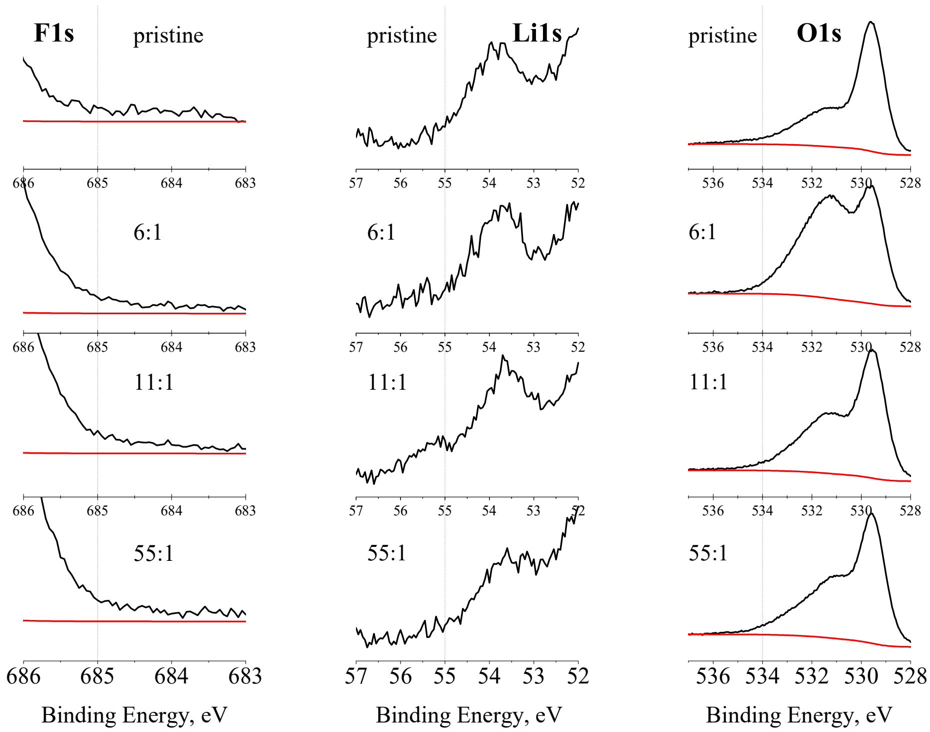

Figure S10. Comparison of F 1s, Li 1s and O 1s spectra of pristine electrodes and electrodes cycled in aqueous solutions.

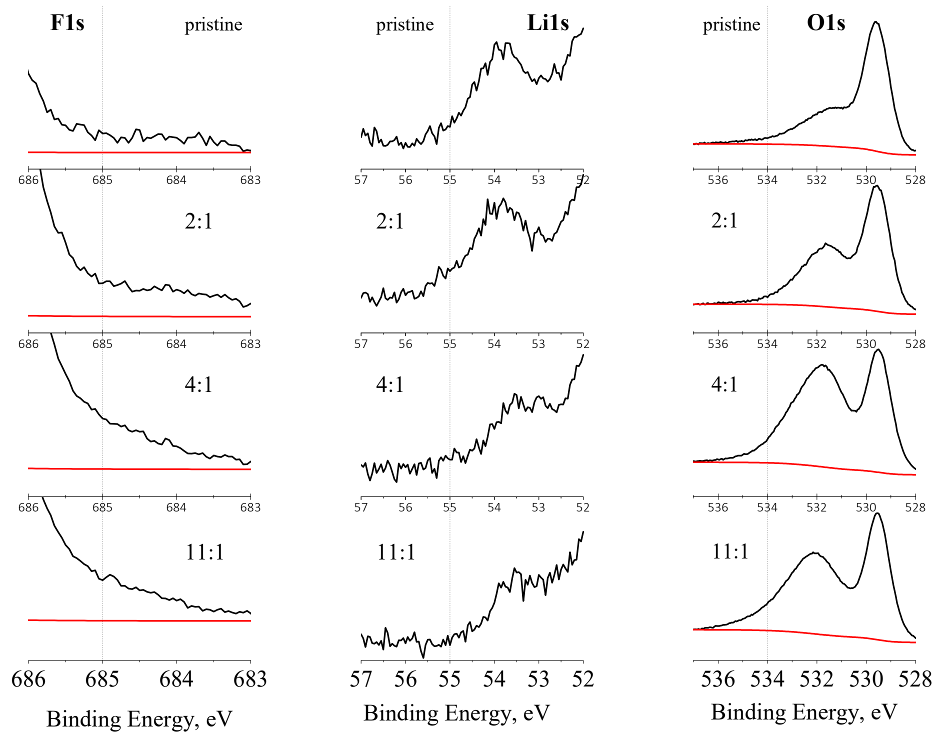

Figure S11. Comparison of F 1s, Li 1s and O 1s spectra of pristine electrodes and electrodes cycled in carbonate solutions.

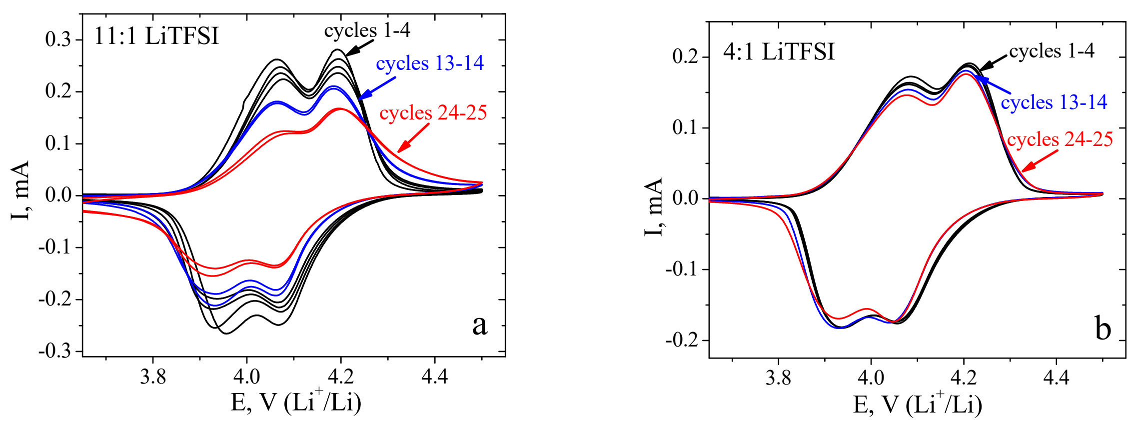

Figure S12. Cyclic voltammograms (first 25 cycles) of $LiMn_2O_4$ electrodes in 11:1 and 4:1 EC-DEC/LiTFSI solutions. Scan rate is 100 $\mu V \cdot s^{-1}$.