ADDITIONAL DATA

Table 1: Hyperfine parameters obtained in the refinement of all ^{57}Fe Mössbauer spectra for the $LiMn_{0.25}Fe_{0.75}PO_4$ electrode in the in situ cell during the charge (isomer shift (δ), quadrupole splitting (Δ) and Mössbauer relative contributions (%)

$x(Li^+)$	$LiMn^{II}_{0.25}Fe^{II}_{0.75}PO_4$			$Li_{0.55}Mn^{II}_{0.25}Fe^{II}_{0.75}PO_4$			$Li_{0.55}Mn^{II}_{0.25}Fe^{III}_{0.75}PO_4$			$Mn^{III}_{0.25}Fe^{III}_{0.75}PO_4$			$Li_{0.25}Mn^{II}_{0.25}Fe^{III}_{0.75}PO_4$		
	δ mm/s	Δ mm/s	%	δ mm/s	Δ mm/s	%	δ mm/s	Δ mm/s	%	δ mm/s	Δ mm/s	%	δ mm/s	Δ mm/s	%
1.00	1.227	2.96	100	-	-	-	-	-	-	-	-	-	-	-	-
0.95	1.226	2.95	95	-	-	-	0.448	1.08	5	-	-	-	-	-	-
0.90	1.227	2.95	80	1.283	2.72	10	0.448	1.08	10	-	-	-	-	-	-
0.84	1.226	2.95	66	1.278	2.71	18	0.448	1.06	16	-	-	-	-	-	-
0.79	1.226	2.95	47	1.288	2.71	29	0.435	1.08	24	-	-	-	-	-	-
0.74	1.220	2.94	38	1.286	2.71	33	0.444	1.02	29	-	-	-	-	-	-
0.69	1.221	2.95	23	1.280	2.72	38	0.438	1.10	39	-	-	-	-	-	-
0.64	1.224	2.94	12	1.279	2.71	41	0.437	1.10	47	-	-	-	-	-	-
0.58	1.221	2.92	2	1.275	2.71	44	0.434	1.11	54	-	-	-	-	-	-
0.53	-	-	-	1.286	2.71	39	0.435	1.18	61	-	-	-	-	-	-
0.48	-	-	-	1.275	2.71	25	0.434	1.21	75	-	-	-	-	-	-
0.43	-	-	-	1.288	2.71	24	0.437	1.25	76	-	-	-	-	-	-
0.37	-	-	-	1.286	2.72	17	0.442	1.29	83	-	-	-	-	-	-
0.32	-	-	-	1.280	2.71	18	0.442	1.30	82	-	-	-	-	-	-
0.25	-	-	-	-	-	-	-	-	-	0.410	1.52	40	0.418	1.30	60
0.22	-	-	-	-	-	-	-	-	-	0.410	1.52	60	0.418	1.30	40
0.17	-	-	-	-	-	-	-	-	-	0.412	1.52	80	0.421	1.30	20
0.11	-	-	-	-	-	-	-	-	-	0.413	1.52	90	0.430	1.30	10

Table 2: Hyperfine parameters obtained in the refinement of all ^{57}Fe Mössbauer spectra for the $LiFePO_4$ electrode in the in situ cell during the charge (isomer shift (δ), quadrupole splitting (Δ) and Mössbauer relative contributions (%)

$x(Li^+)$	$LiFe^{II}PO_4$			$Fe^{III}PO_4$		
	δ mm/s	Δ mm/s	%	δ mm/s	Δ mm/s	%
1.00	1.223	2.959	100	-	-	-
0.95	1.223	2.959	94	0.401	1.518	6
0.90	1.218	2.943	90	0.409	1.518	10
0.84	1.220	2.976	84	0.410	1.523	16
0.79	1.218	2.951	80	0.403	1.516	20
0.74	1.219	2.943	76	0.407	1.499	24
0.69	1.218	2.939	70	0.399	1.514	30
0.64	1.219	2.930	66	0.392	1.517	34
0.58	1.218	2.940	57	0.407	1.495	42
0.53	1.221	2.948	54	0.408	1.513	46
0.48	1.216	2.922	47	0.407	1.528	53
0.43	1.226	2.924	41	0.416	1.525	59
0.37	1.221	2.921	35	0.412	1.524	65
0.32	1.218	2.922	27	0.410	1.530	73
0.25	1.221	2.921	23	0.411	1.530	77
0.22	1.218	2.928	18	0.414	1.524	82
0.17	1.224	2.919	12	0.418	1.528	88
0.11	1.223	2.925	5	0.412	1.530	95