Electronic Supplementary Information

Solution-based chemical pre-alkaliation of metal-ion battery cathode materials for increased capacity

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Table S1. Active material mass loadings of electrodes.

Material	Electrode purpose	Weight ratio of AM:SP:CMC	Active material mass loading, mg cm^{-2}
PQI	Electrochemical tests	6:3:1	1.4
PQI	FTIR measurements	9:0:1 (no SP)	0.7
$Li_3V_2(PO_4)_3$	Electrochemical tests	7:2:1	1.3
$Li_3V_2(PO_4)_3$	XRD measurements	9:0:1 (no SP)	4.1
$Li_3V_2(PO_4)_3$	XRD measurements after electrochemical pre-lithiation	8:1:1	3.9
$Na_3V_2(PO_4)_3$	Electrochemical tests	7:2:1	1.3
$Na_3V_2(PO_4)_3$	XRD measurements	8:1:1	5.0
$LiMn_{1.5}Ni_{0.5}O_4$	Electrochemical tests, XRD measurements	8:1:1	3.0

Table S2. Potential ranges for the galvanostatic cycling of pristine and pre-alkaliated materials.

Material	Potential range (V vs. M^+/M), anode
PQI	1.1-3.6, K
$Li_3V_2(PO_4)_3$	1.2-4.2, Li
$Na_3V_2(PO_4)_3$	0.9-3.9, Na
$LiMn_{1.5}Ni_{0.5}O_4$	3.0-4.9, Li

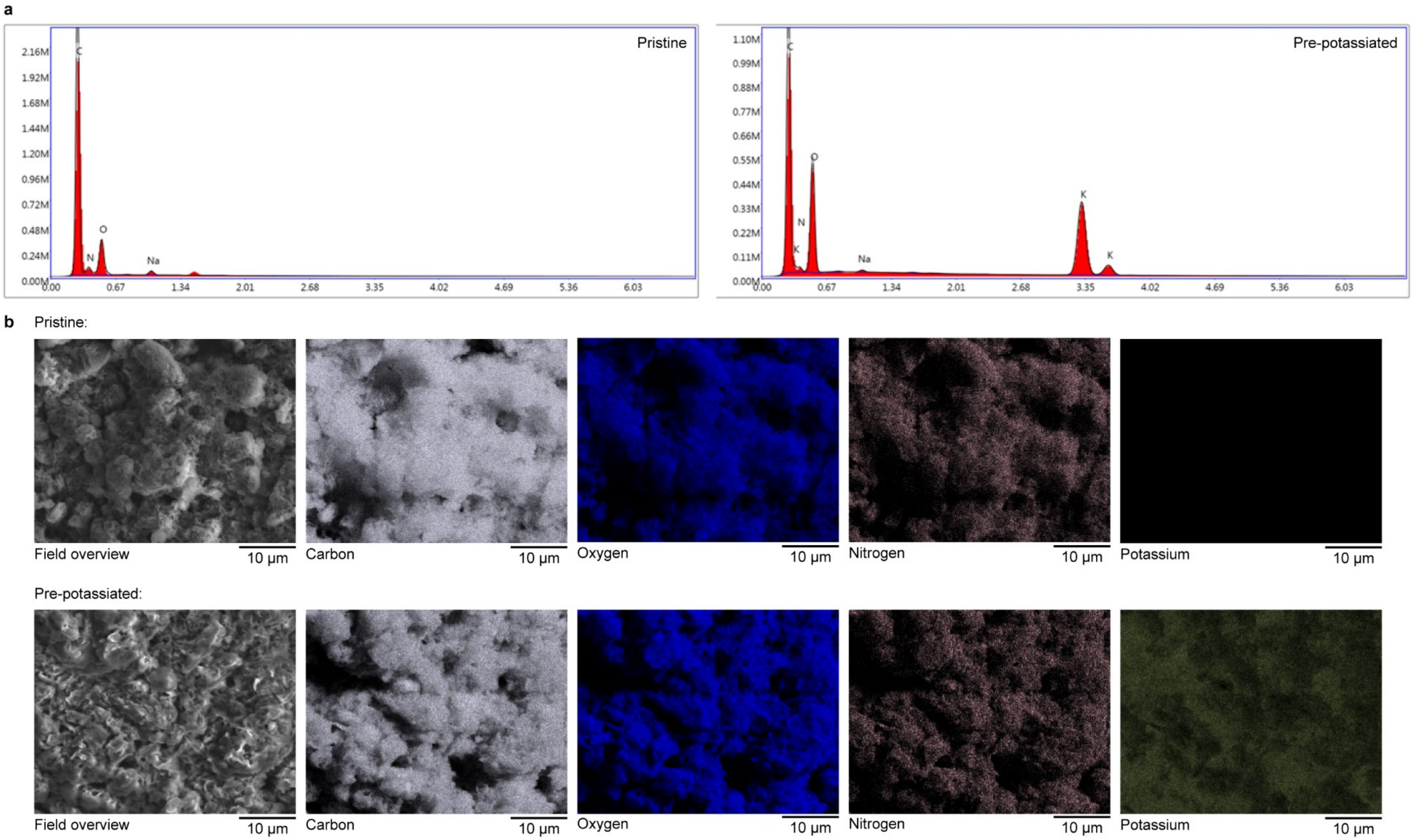

Fig. S1. Averaged EDX spectra (a) and EDX element mapping (b) for pristine and pre-potassiated **PQI**-based electrodes.

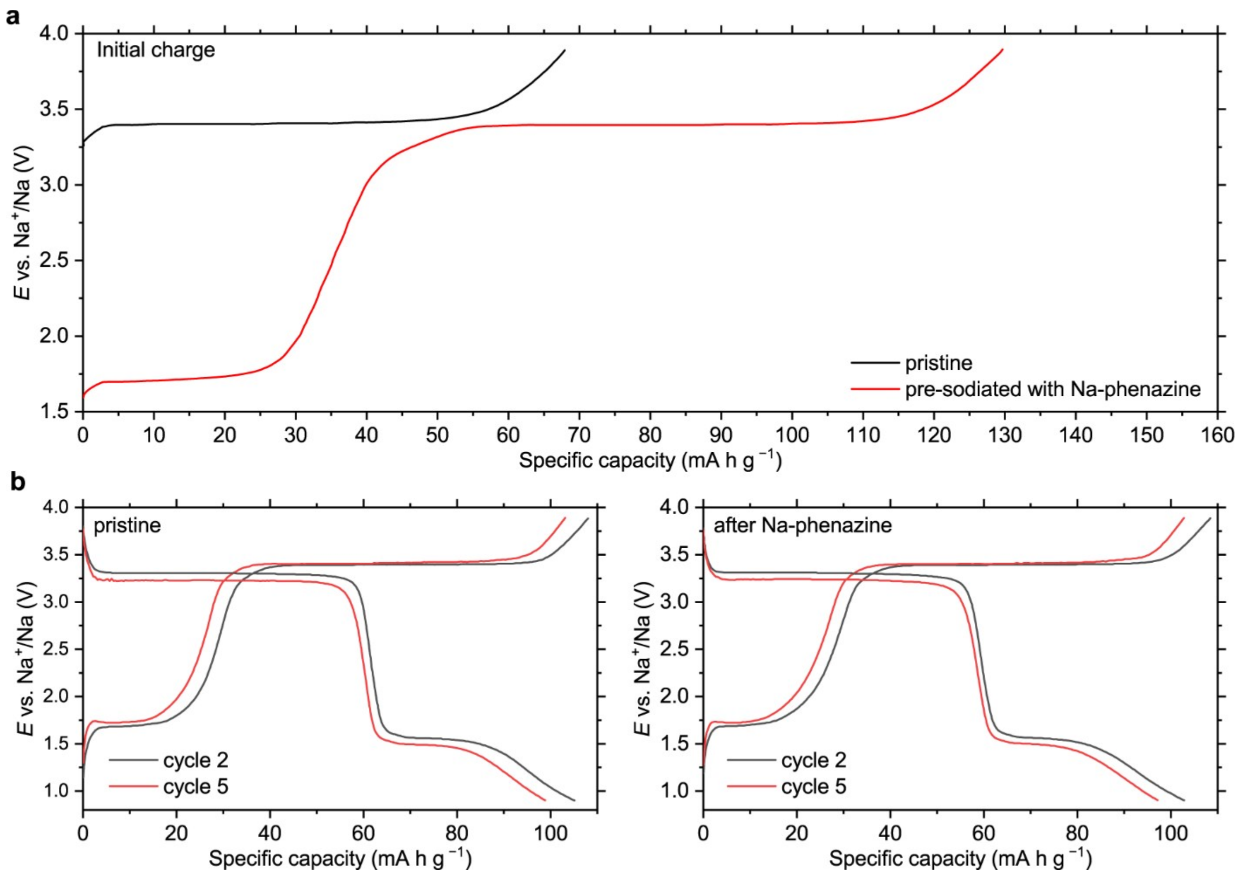

Fig. S2. Initial charge curves for pristine $Na_3V_2(PO_4)_3$ and the material pre-metalated with sodium phenazenide at 0.1 A g^{-1} (a); charge-discharge profiles of the materials for 2nd and 5th cycles at 0.1 A g^{-1} (b).

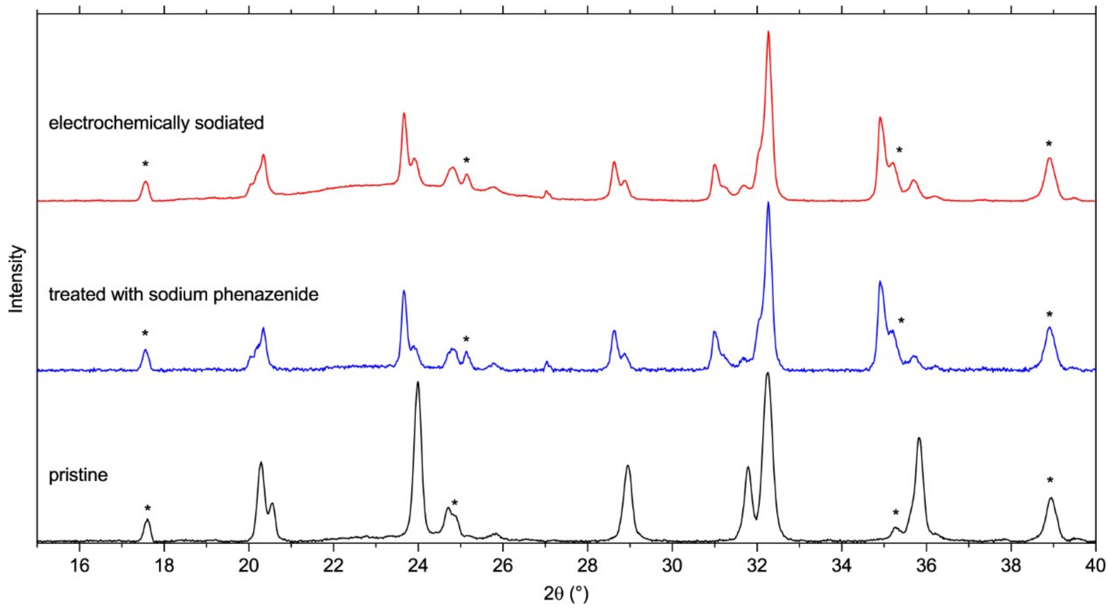

Fig. S3. Baseline-corrected X-ray diffraction patterns of $Na_3V_2(PO_4)_3$, the material treated with sodium phenazenide and $Na_3V_2(PO_4)_3$ discharged to 1.2 V vs. Na^+/Na. XRD pattern regions where background peaks appear are marked with "*".

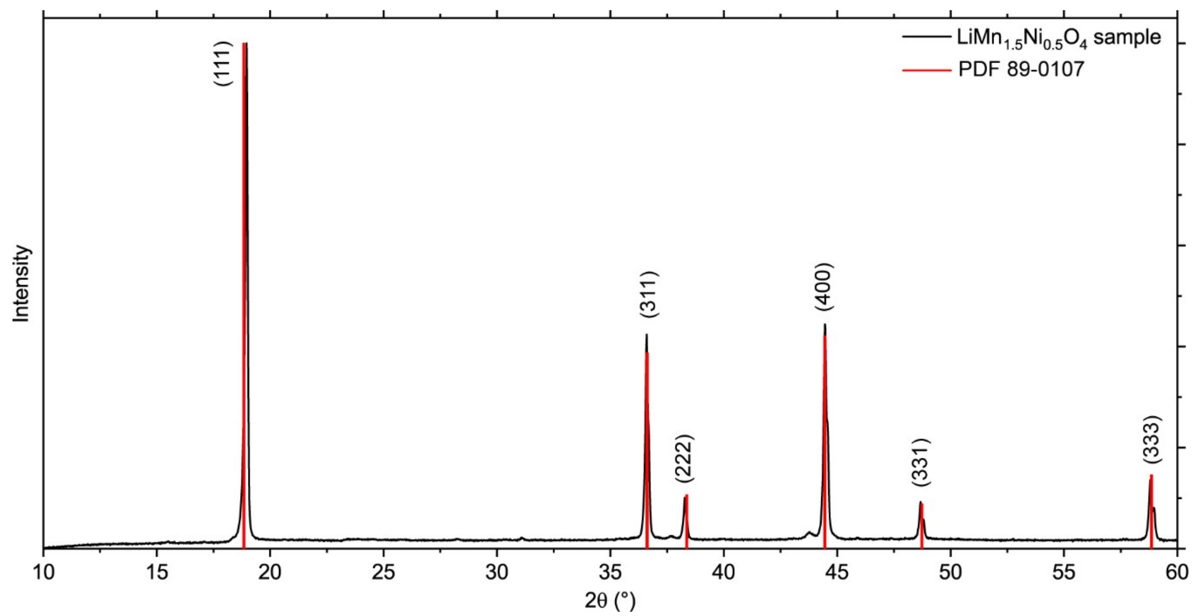

Fig. S4. XRD pattern of as-synthesized $LiMn_{1.5}Ni_{0.5}O_4$ and reference XRD peaks from PDF ICDD (no. 89-0107). Miller indices of the peaks are indicated.

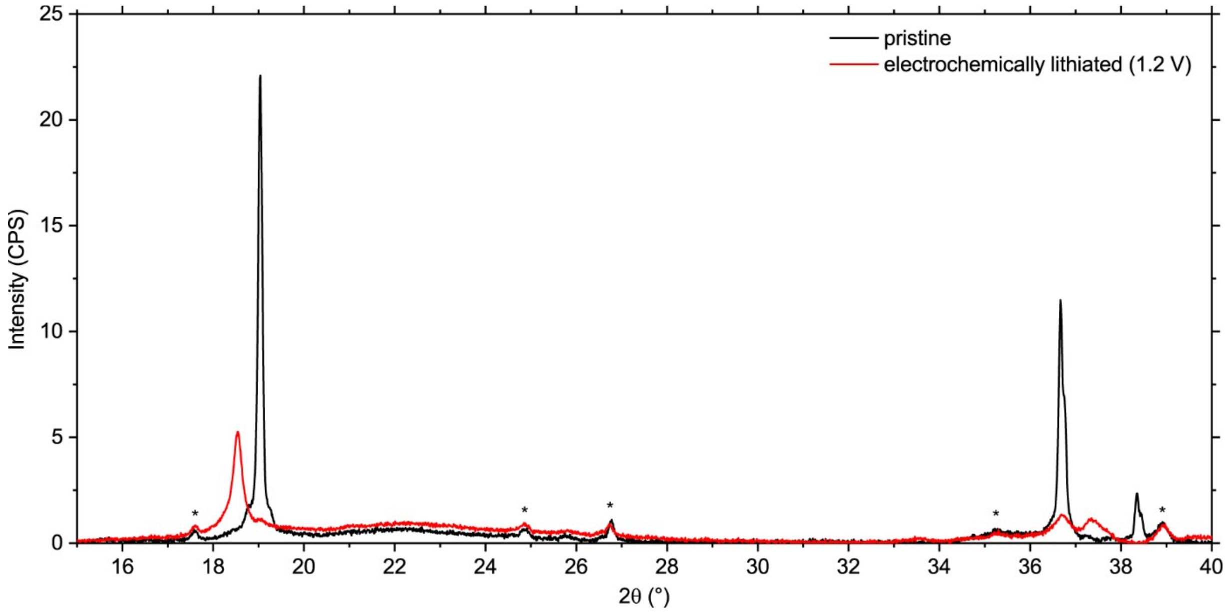

Fig. S5. Baseline-corrected X-ray diffraction patterns of pristine $LiMn_{1.5}Ni_{0.5}O_4$ and $LiMn_{1.5}Ni_{0.5}O_4$ discharged to 1.2 V vs. Li^+/Li. XRD pattern regions where background peaks appear are marked with "*".

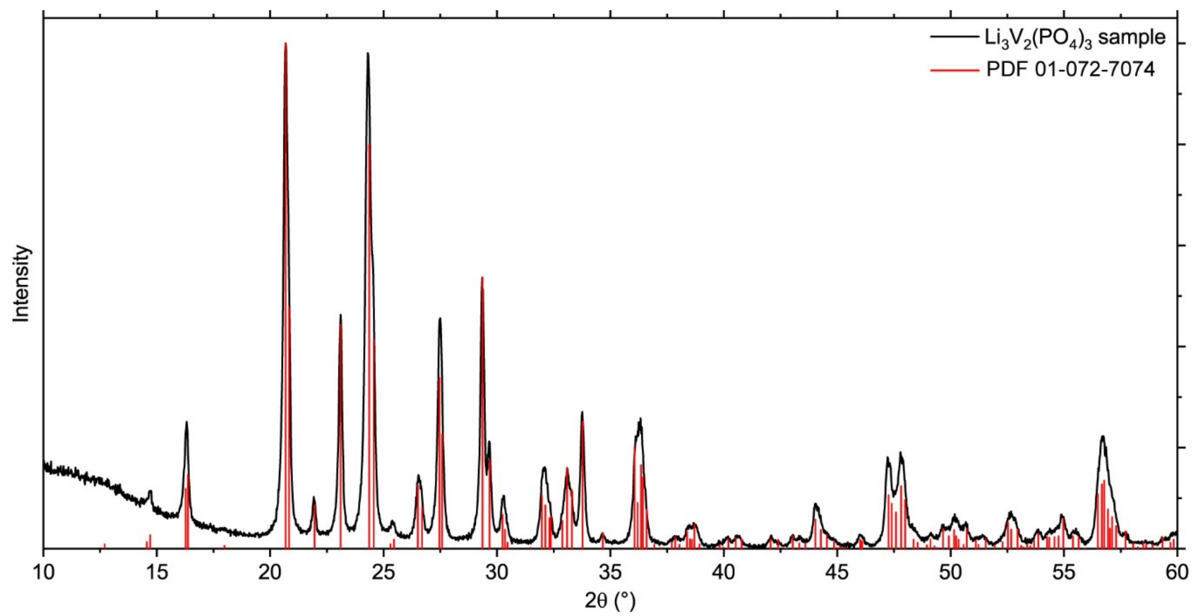

Fig. S6. XRD pattern of as-synthesized $Li_3V_2(PO_4)_3$ and XRD peaks for $Li_3V_2(PO_4)_3$ from PDF-2 ICDD (no. 01-072-7074).

Table S3. Miller indices of $Li_3V_2(PO_4)_3$ according to PDF-2 no. 01-072-7074.

d(Å)	2θ (°)	Intensity	h	k	l
6.9652	12.699	11	0	1	1
6.9652	12.699	11	1	0	1
6.07999	14.557	15	1	1	0
6.01816	14.708	29	0	0	2
5.44339	16.271	120	-1	1	1
5.41058	16.37	148	1	1	1
4.9292	17.981	8	0	1	2
4.29332	20.672	1000	0	2	0
4.29332	20.672	1000	-1	1	2
4.2612	20.829	478	1	1	2
4.04588	21.951	88	0	2	1
3.84712	23.101	445	1	2	0
3.84712	23.101	445	2	1	0
3.65118	24.359	800	-1	0	3
3.65118	24.359	800	2	1	1
3.62158	24.561	414	1	0	3
3.5178	25.297	11	-2	0	2
3.49646	25.454	20	0	2	2
3.36034	26.504	127	-1	1	3
3.33721	26.691	83	1	1	3
3.24627	27.453	340	-2	1	2
3.24627	27.453	340	-1	2	2
3.23231	27.574	228	2	1	2
3.23231	27.574	228	1	2	2
3.03999	29.356	538	2	2	0
3.00908	29.665	176	0	0	4
2.95271	30.244	69	-2	2	1
2.9422	30.355	40	2	2	1
2.93217	30.461	14	0	2	3
2.83994	31.476	4	0	1	4
2.79695	31.973	107	-3	0	1
2.78357	32.13	88	-1	2	3
2.78357	32.13	88	3	0	1
2.76891	32.305	62	1	2	3
2.76373	32.367	66	2	1	3
2.72169	32.881	57	1	3	0
2.72169	32.881	57	-2	2	2
2.70529	33.086	162	-1	1	4
2.70529	33.086	162	2	2	2

2.68885	33.295	118	1	1	4
2.65256	33.764	253	1	3	1
2.65256	33.764	253	-1	3	1
2.58602	34.66	32	0	3	2
2.4886	36.062	204	-3	1	2
2.47972	36.196	93	-2	0	4
2.47972	36.196	93	-1	3	2
2.46984	36.345	167	3	1	2
2.46984	36.345	167	1	3	2
2.4646	36.425	143	0	2	4
2.45365	36.594	80	2	0	4
2.43181	36.934	10	-2	2	3
2.41429	37.212	4	2	2	3
2.38405	37.702	14	-2	1	4
2.38405	37.702	14	2	3	0
2.37481	37.854	25	-1	2	4
2.36389	38.036	10	1	2	4
2.34392	38.372	35	-2	3	1
2.34392	38.372	35	-3	2	1
2.33603	38.507	21	2	3	1
2.33603	38.507	21	3	2	1
2.33097	38.594	20	0	3	3
2.32468	38.702	50	3	0	3
2.32468	38.702	50	-1	0	5
2.31189	38.925	11	1	0	5
2.26243	39.812	10	-3	1	3
2.2534	39.978	5	-1	3	3
2.24134	40.202	21	3	1	3
2.24134	40.202	21	-1	1	5
2.22437	40.522	24	-2	3	2
2.22437	40.522	24	-3	2	2
2.21094	40.779	20	3	2	2
2.21094	40.779	20	2	3	2
2.14666	42.058	21	-2	2	4
2.14666	42.058	21	0	4	0
2.1306	42.39	20	2	2	4
2.11452	42.728	3	0	4	1
2.10002	43.038	27	0	2	5
2.08685	43.323	13	1	4	0
2.08685	43.323	13	4	1	0
2.07451	43.594	13	0	3	4
2.05484	44.033	60	1	4	1
2.05484	44.033	60	-2	3	3

2.04424	44.273	39	3	2	3
2.04424	44.273	39	2	3	3
2.0326	44.54	29	2	1	5
2.0326	44.54	29	-4	0	2
2.01895	44.858	15	4	0	2
2.01895	44.858	15	-1	3	4
2.01337	44.989	4	1	3	4
2.00807	45.114	7	0	0	6
2.00807	45.114	7	3	1	4
2.00099	45.282	3	-3	3	1
1.99608	45.4	3	3	3	1
1.97083	46.015	20	-1	4	2
1.96769	46.093	17	4	1	2
1.96769	46.093	17	1	4	2
1.95351	46.447	2	0	1	6
1.92176	47.26	108	2	4	0
1.92176	47.26	108	4	2	0
1.91633	47.402	91	3	3	2
1.90931	47.587	74	-1	1	6
1.90079	47.814	126	-2	4	1
1.90079	47.814	126	1	1	6
1.89416	47.992	99	-2	2	5
1.89416	47.992	99	2	4	1
1.88036	48.366	20	-3	2	4
1.88036	48.366	20	2	2	5
1.87402	48.541	14	-2	3	4
1.85925	48.951	9	-4	1	3
1.85925	48.951	9	3	2	4
1.85367	49.108	21	-1	4	3
1.85367	49.108	21	-3	0	5
1.84744	49.285	7	1	4	3
1.84275	49.419	4	0	3	5
1.84275	49.419	4	4	1	3
1.83436	49.66	42	-2	4	2
1.83436	49.66	42	3	0	5
1.82559	49.915	27	-2	0	6
1.82559	49.915	27	4	2	2
1.81764	50.148	39	0	2	6
1.81446	50.242	27	-3	3	3
1.81079	50.351	20	2	0	6
1.81079	50.351	20	-3	1	5
1.80353	50.568	10	3	3	3
1.80353	50.568	10	-1	3	5

1.7989	50.708	42	1	3	5
1.78572	51.109	18	-2	1	6
1.78187	51.227	10	-1	2	6
1.77186	51.538	22	2	1	6
1.7589	51.946	9	-4	0	4
1.74823	52.287	15	0	4	4
1.74098	52.521	54	-4	2	3
1.74098	52.521	54	4	0	4
1.73641	52.67	40	-2	4	3
1.72812	52.942	40	4	2	3
1.72812	52.942	40	2	4	3
1.72316	53.106	8	-4	1	4
1.72006	53.21	5	3	4	0
1.72006	53.21	5	4	3	0
1.7153	53.369	10	-1	4	4
1.71117	53.508	7	1	4	4
1.70624	53.675	18	-4	3	1
1.70624	53.675	18	-5	0	1
1.70073	53.863	32	-2	3	5
1.70073	53.863	32	4	3	1
1.6896	54.247	25	2	3	5
1.6896	54.247	25	-1	0	7
1.68683	54.343	24	-3	3	4
1.68683	54.343	24	3	2	5
1.68017	54.576	25	-2	2	6
1.67513	54.754	27	-5	1	1
1.67513	54.754	27	3	3	4
1.66927	54.963	60	1	5	1
1.66927	54.963	60	-1	5	1
1.65756	55.384	27	-3	4	2
1.65756	55.384	27	-4	3	2
1.65039	55.646	25	4	3	2
1.65039	55.646	25	3	4	2
1.64307	55.915	3	0	3	6
1.62775	56.488	110	-4	2	4
1.62775	56.488	110	-5	1	2
1.62313	56.664	129	1	5	2
1.62313	56.664	129	-2	4	4
1.62045	56.766	137	5	1	2
1.61616	56.93	80	2	4	4
1.61616	56.93	80	-1	3	6
1.61377	57.022	42	4	2	4
1.61133	57.117	65	1	3	6

1.6069	57.289	47	3	1	6
1.59635	57.703	37	2	5	0
1.59635	57.703	37	0	2	7
1.58777	58.044	13	-5	2	1
1.58777	58.044	13	-5	0	3
1.58275	58.246	5	2	5	1
1.58275	58.246	5	-2	5	1
1.57668	58.492	14	5	0	3
1.57668	58.492	14	3	4	3
1.57359	58.618	10	-1	2	7
1.57359	58.618	10	1	4	5
1.5668	58.897	10	1	2	7
1.56134	59.123	3	-5	1	3
1.55615	59.34	25	-1	5	3
1.55615	59.34	25	-3	3	5
1.5479	59.688	14	-5	2	2
1.5479	59.688	14	5	1	3
1.54467	59.826	20	-2	5	2
1.54467	59.826	20	3	3	5

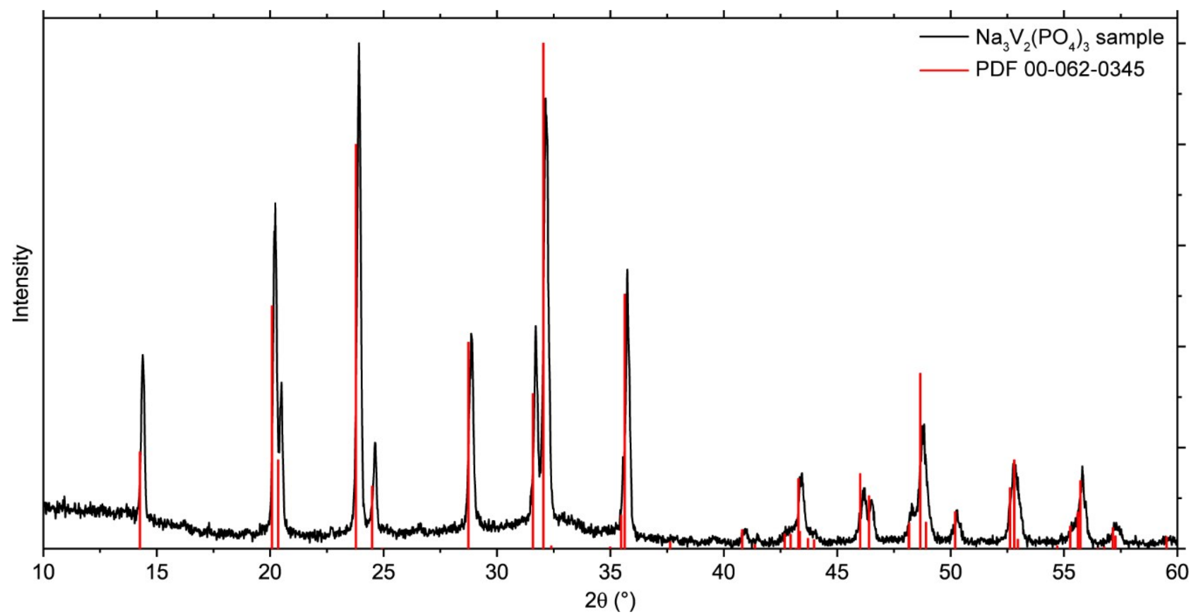

Fig. S7. XRD pattern of as-synthesized $Na_3V_2(PO_4)_3$ and XRD peaks for $Na_3V_2(PO_4)_3$ from PDF-2 ICDD (no. 00-062-0345).

Table S4. Miller indices of $Na_3V_2(PO_4)_3$ according to PDF-2 no. 00-062-0345.

d(Å)	2θ (°)	Intensity	h	k	l
6.20804	14.255	193	0	1	2
4.41903	20.078	481	1	0	4
4.36142	20.346	177	1	1	0
3.73924	23.777	800	1	1	3
3.63225	24.488	125	0	0	6
3.56884	24.93	3	2	0	2
3.1041	28.737	409	0	2	4
2.83101	31.578	308	2	1	1
2.79106	32.042	1000	1	1	6
2.76194	32.389	7	1	2	2
2.56264	34.986	5	0	1	8
2.52898	35.467	68	2	1	4
2.51805	35.626	504	3	0	0
2.38843	37.63	15	1	2	5
2.20945	40.808	39	2	0	8
2.18073	41.37	10	2	2	0
2.11706	42.674	31	1	1	9
2.10428	42.946	30	2	1	7
2.09397	43.168	3	1	0	10
2.08862	43.284	140	2	2	3
2.08555	43.351	36	1	3	1
2.06943	43.706	22	0	3	6
2.05748	43.973	19	3	1	2
1.97098	46.011	150	1	2	8
1.95555	46.395	106	1	3	4
1.88833	48.149	39	3	1	5
1.88767	48.167	52	0	2	10
1.86965	48.661	348	2	2	6
1.86082	48.907	54	0	4	2
1.81611	50.194	75	0	0	12
1.78439	51.149	2	4	0	4
1.73823	52.61	122	1	3	7
1.73236	52.802	177	2	1	10
1.72759	52.959	20	3	2	1
1.71154	53.495	2	2	3	2
1.67656	54.704	7	1	1	12
1.66078	55.268	46	3	1	8
1.65151	55.605	74	3	2	4
1.64845	55.717	136	4	1	0

1.62774	56.489	3	1	2	11
1.62046	56.765	5	2	2	9
1.61042	57.152	43	2	3	5
1.60759	57.262	27	1	4	3
1.55207	59.512	25	0	4	8

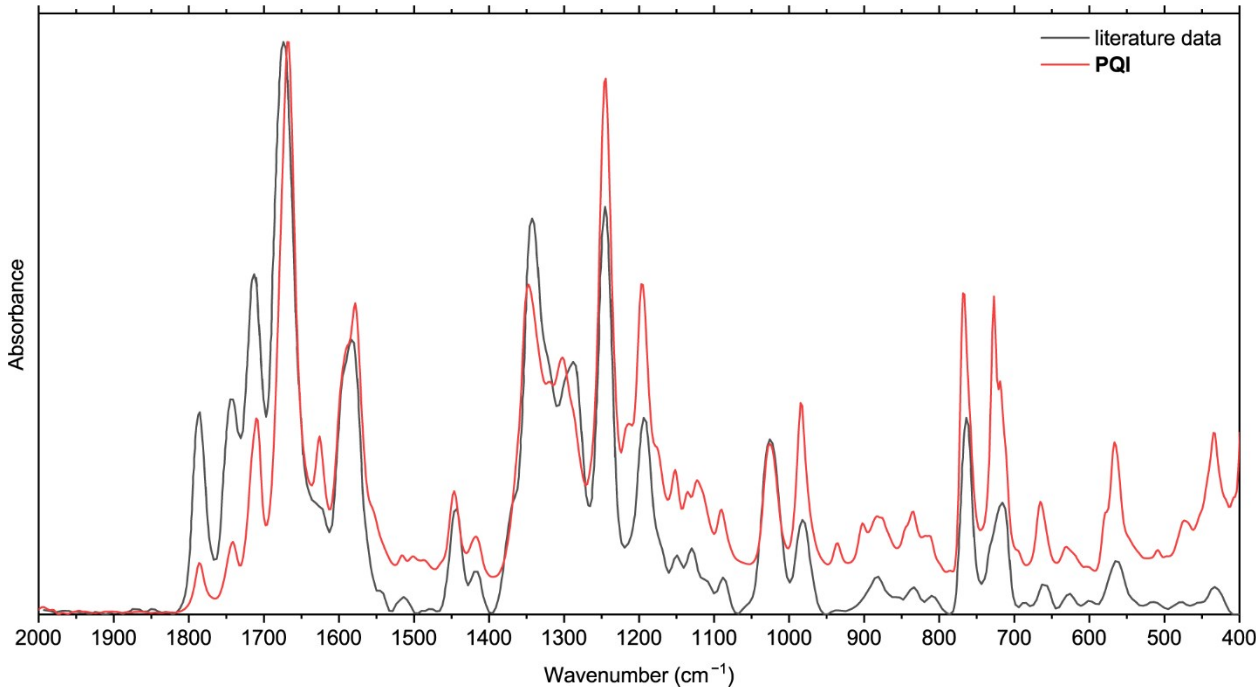

Fig. S8. FTIR spectra of **PQI** compared with the literature data (ref. 63 in the main text).

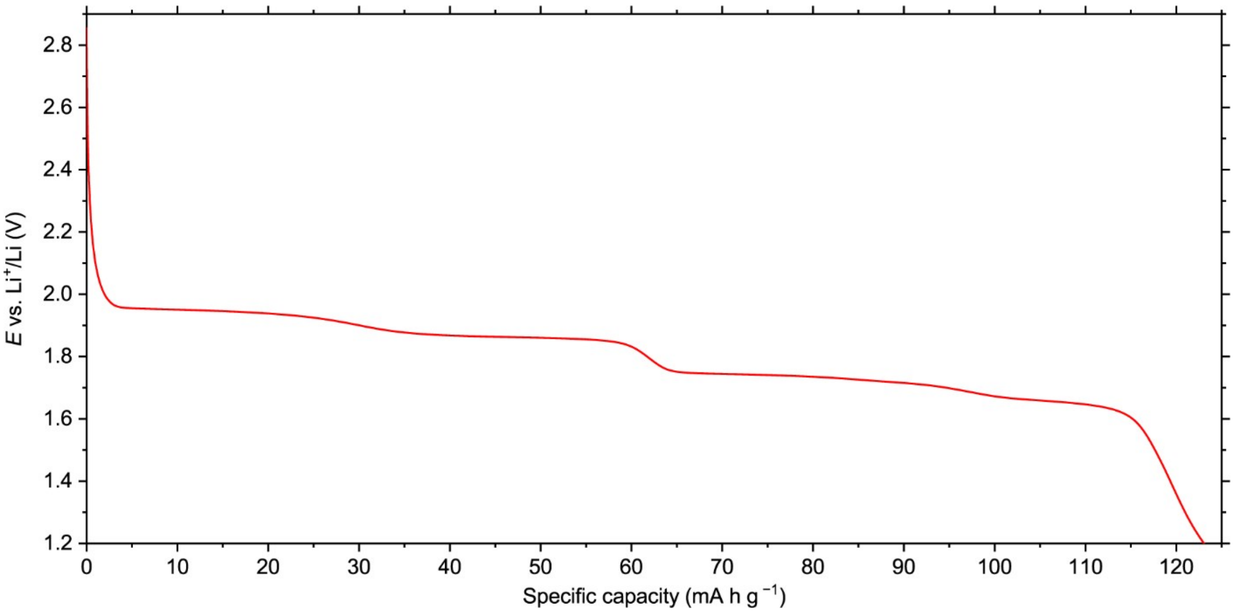

Fig. S9. Discharge curve profile of $Li_3V_2(PO_4)_3$ during electrochemical lithiation for XRD measurements.

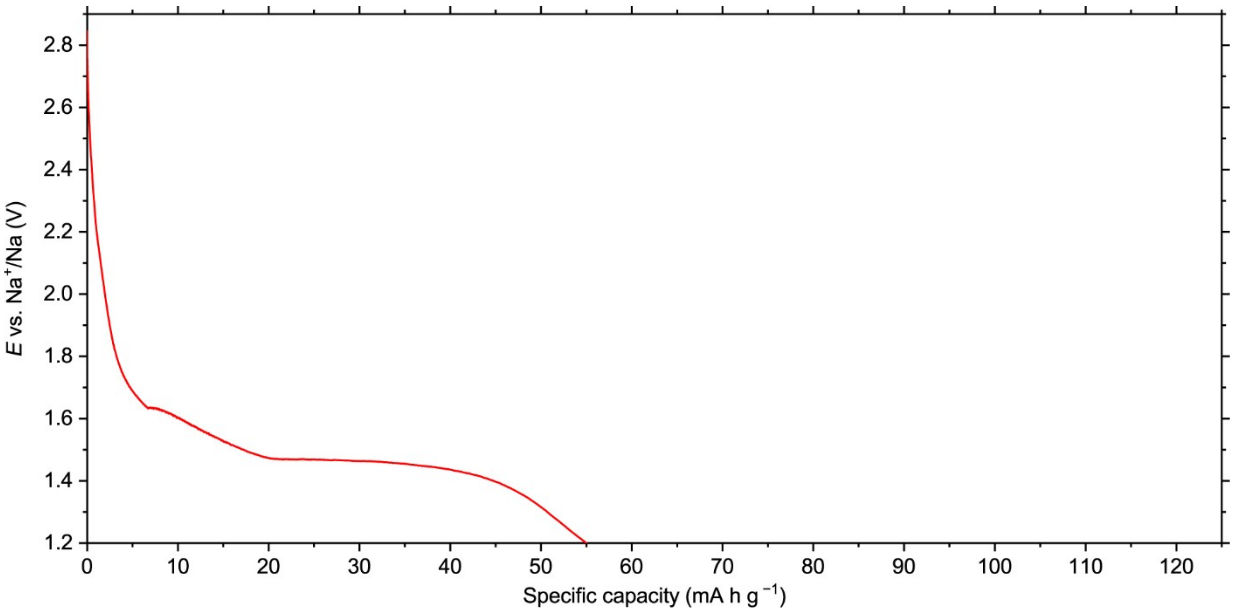

Fig. S10. Discharge curve profile of $Na_3V_2(PO_4)_3$ during electrochemical sodiation for XRD measurements.

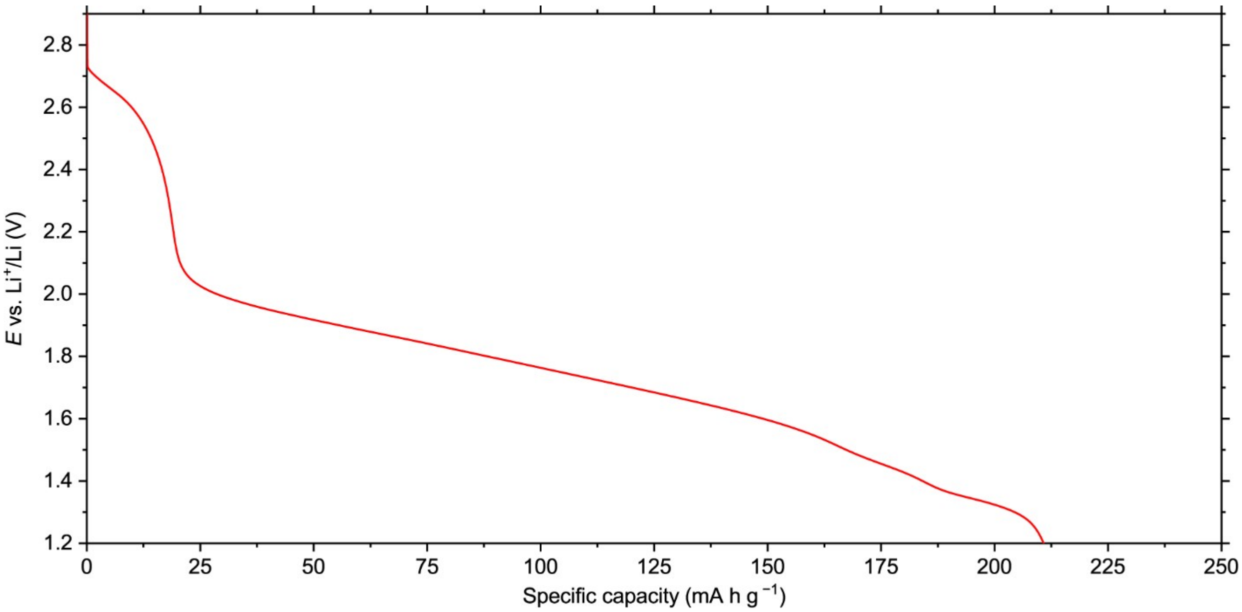

Fig. S11. Discharge curve profile of $LiMn_{1.5}Ni_{0.5}O_4$ during electrochemical lithiation for XRD measurements.

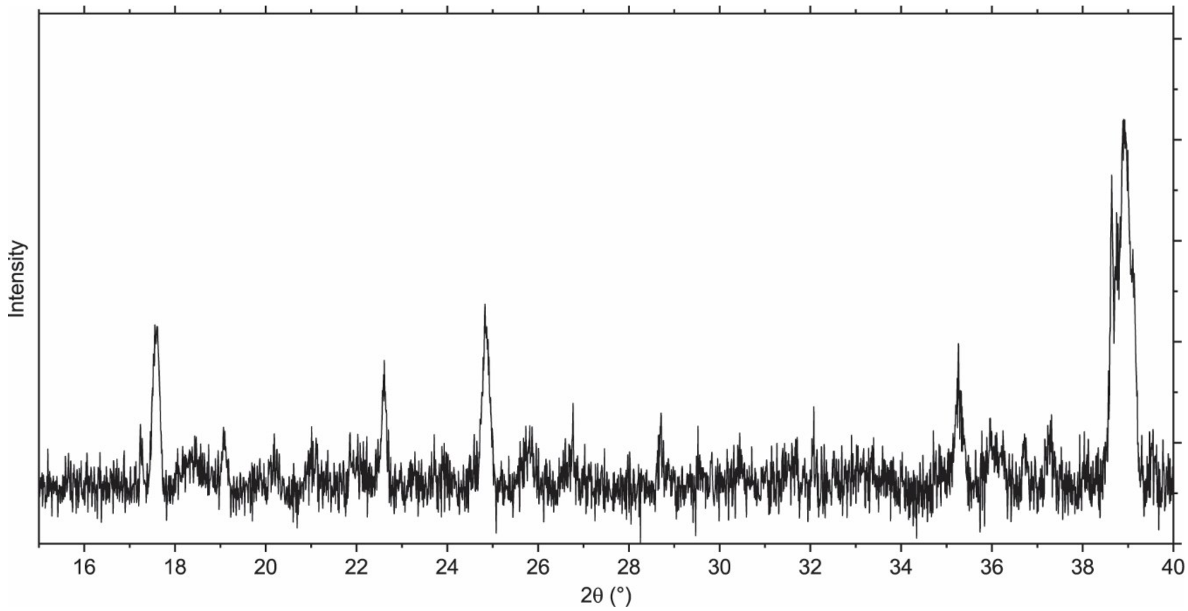

Fig. S12. Baseline-corrected XRD pattern of the cell used for the XRD measurements in inert atmosphere.

Table S5. Redox potentials for the reducing agents used in this study.

Anion/anion-radical	$E_{1/2}$ (V vs. Li^+/Li)	Ref. number from the main text
$[C_{10}H_8]^-$	~0.5	66
$[C_{12}N_2H_8]^-$	~1.9	65
$[C_{12}N_2H_8]^{2-}$	~1.3	65