Electronic Supplementary Information

Nitrogen-doped rock-salt $Li_3V_2O_5$ nanosheet arrays with improved rate capability as anode for thin film lithium-ion microbatteries

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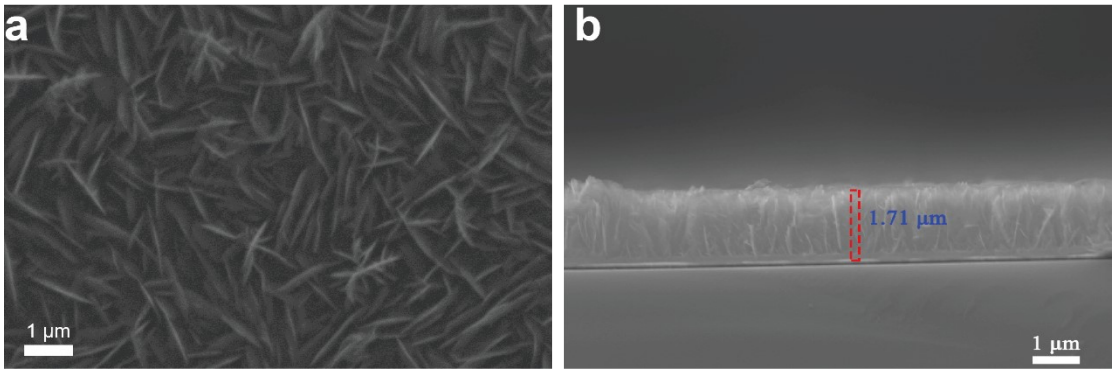


Fig. S1 (a) Top-view FESEM image and (b) cross-sectional FESEM image of the V_2O_5 thin film.

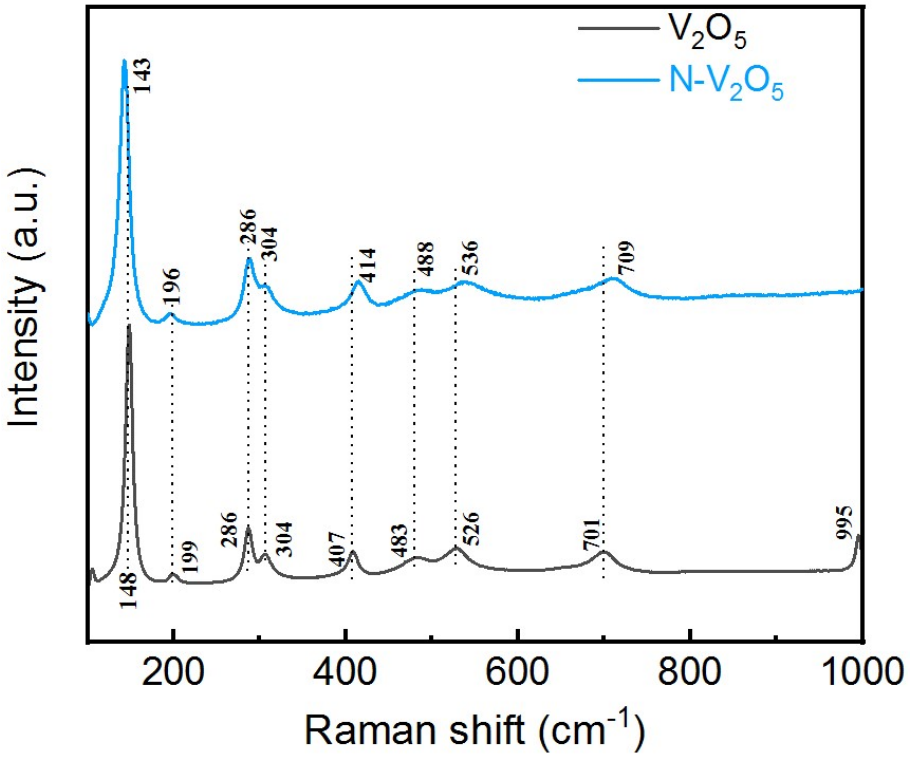


Fig. S2 Raman spectra of the N-V_2O_5 and V_2O_5 thin films.

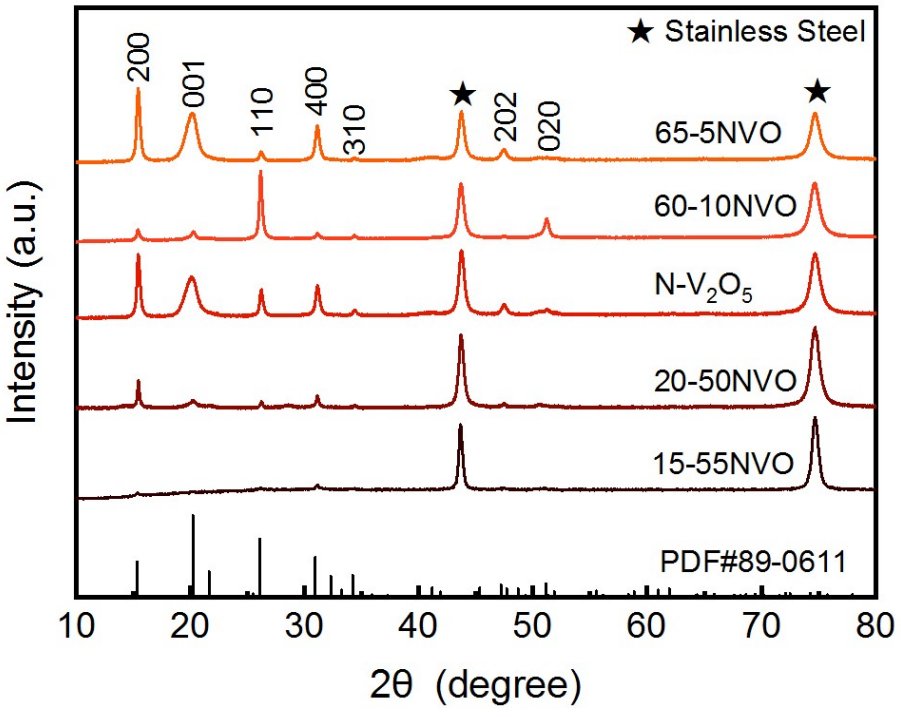


Fig. S3 XRD patterns of the 15-55NVO, 20-50NVO, N-V_2O_5, 60-10NVO, and 65-5NVO thin films.

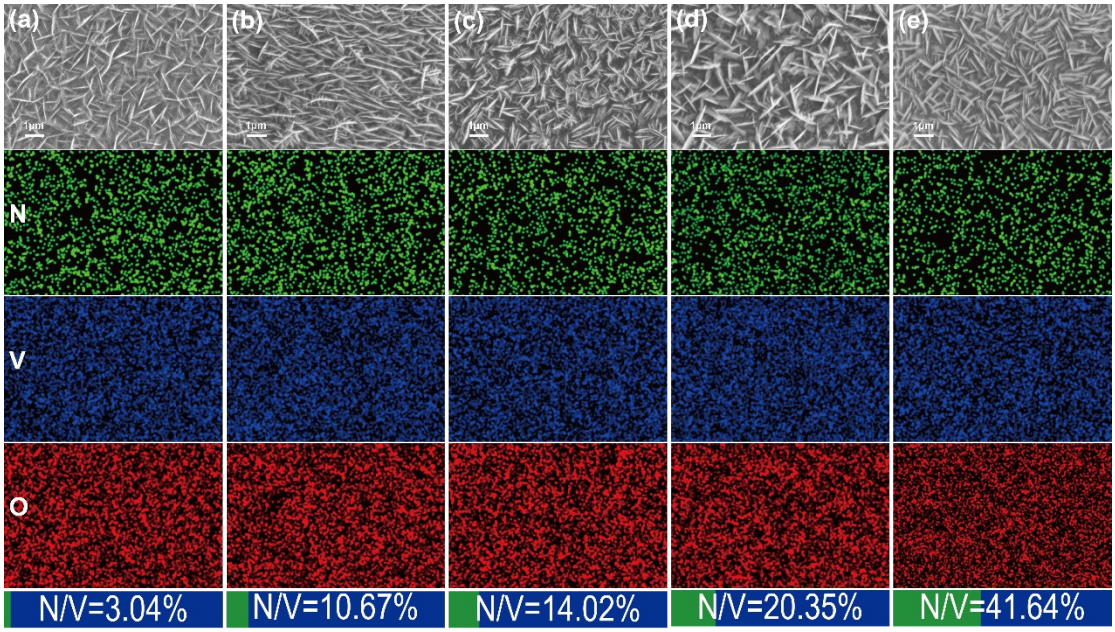


Fig. S4 FESEM images and EDS elemental mapping images of the (a) 15-55NVO, (b) 20-50NVO, (c) N-V_2O_5, (d) 60-10NVO, and (e) 65-5NVO thin films.

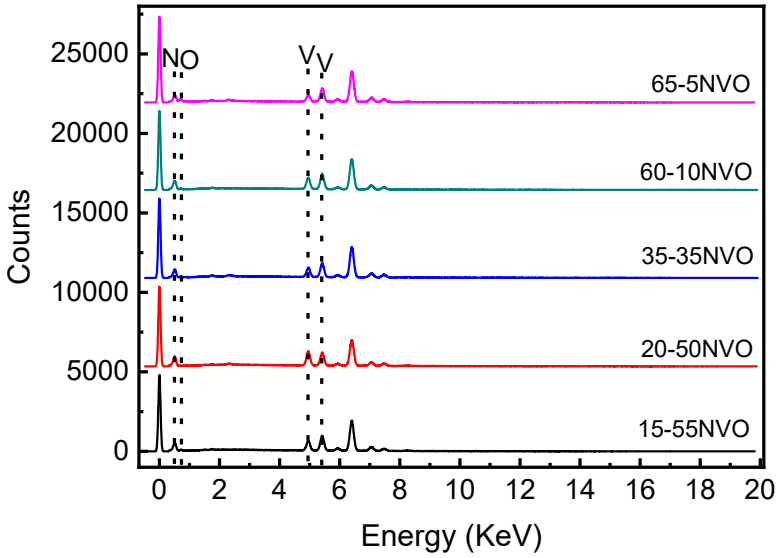


Fig. S5 EDS spectra of the 15-55NVO, 20-50NVO, N-V_2O_5, 60-10NVO, and 65-5NVO thin films.

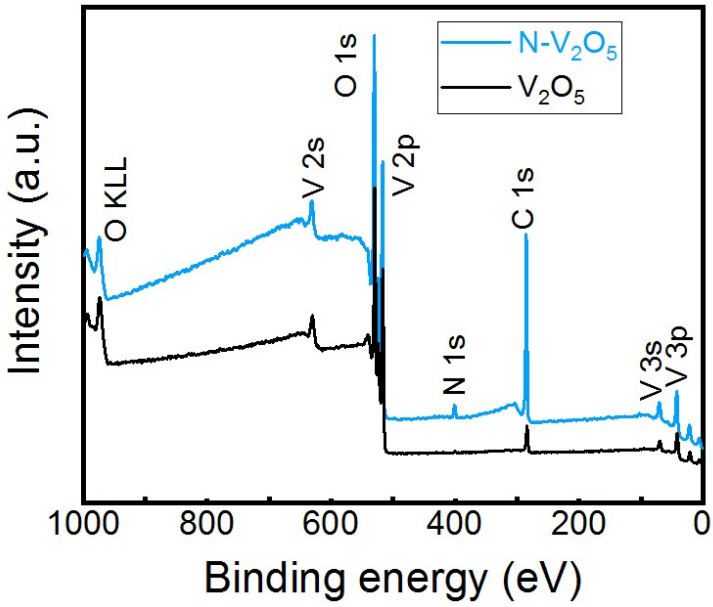


Fig. S6 Survey scan XPS spectra of the N-V_2O_5 and V_2O_5 thin films.

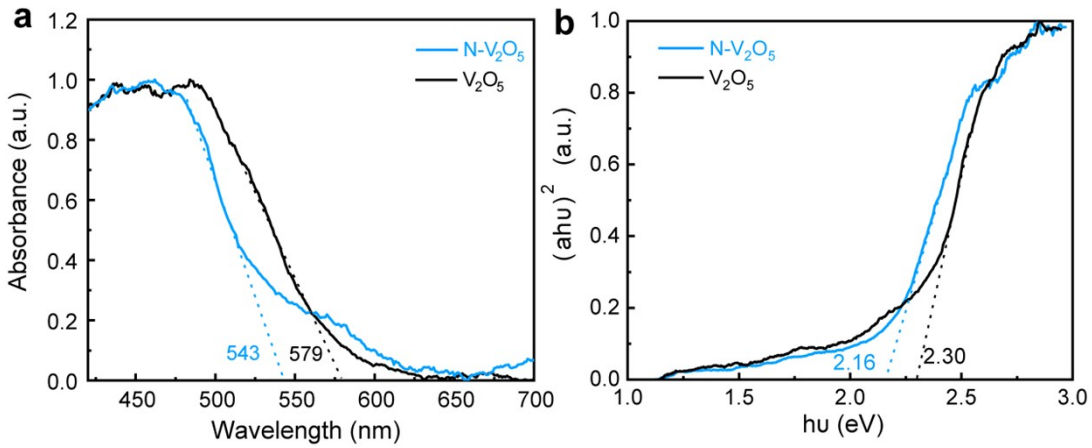


Fig. S7 (a) UV−vis absorption spectra and (b) the transformed Kubelka–Munk function against the photon energy plots of the N-V_2O_5 and V_2O_5 thin films.

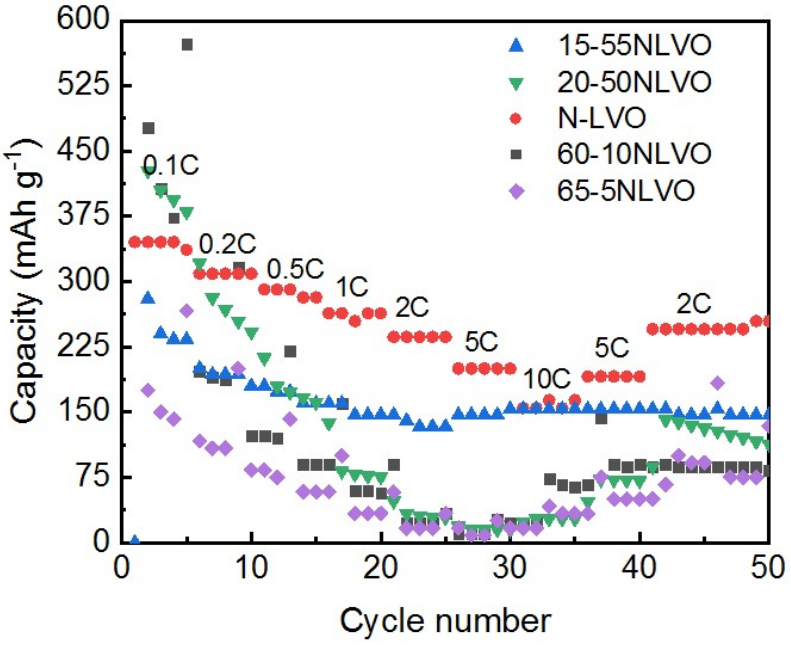


Fig. S8 Rate performances of the 15-55NLVO, 20-50NLVO, N-NLVO, 60-10NLVO, and 65-5NLVO electrodes.

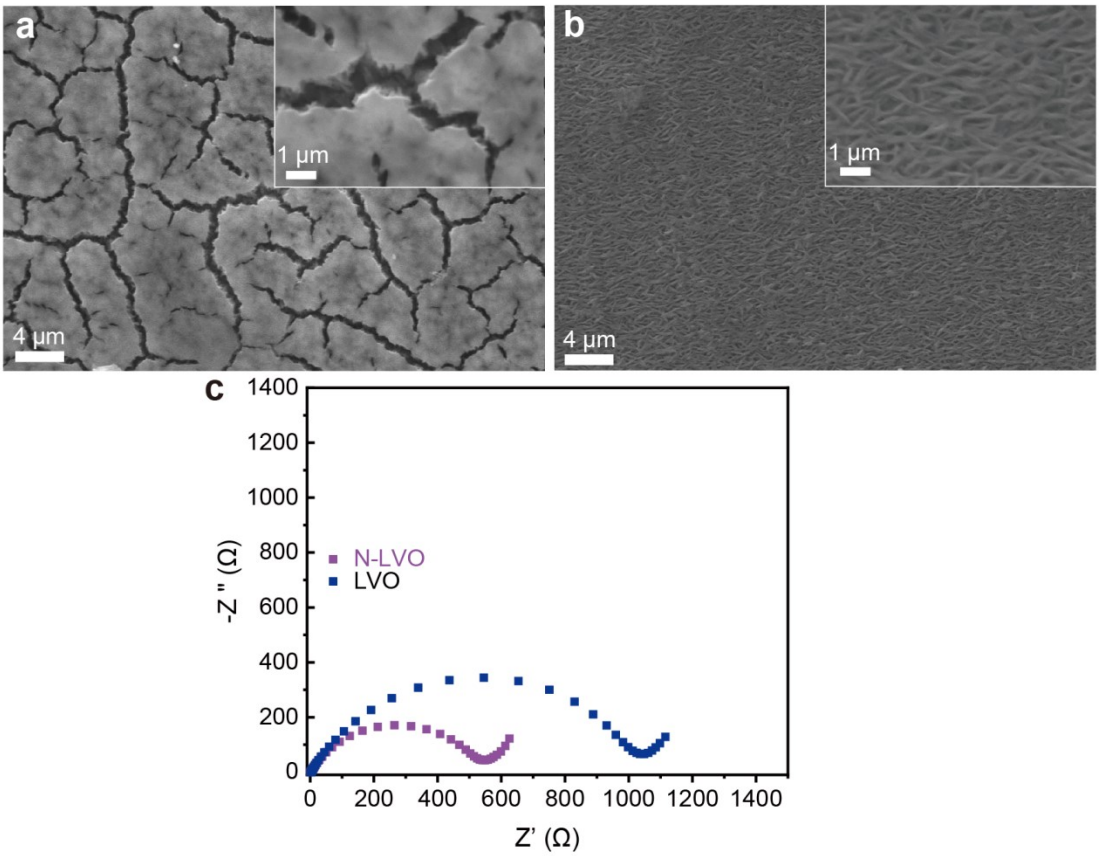


Fig. S9 Top-view FESEM images of the (a) LVO and (b) N-LVO electrodes after 50 cycles. (c) EIS spectra of the LVO and N-LVO electrodes after 50 cycles.

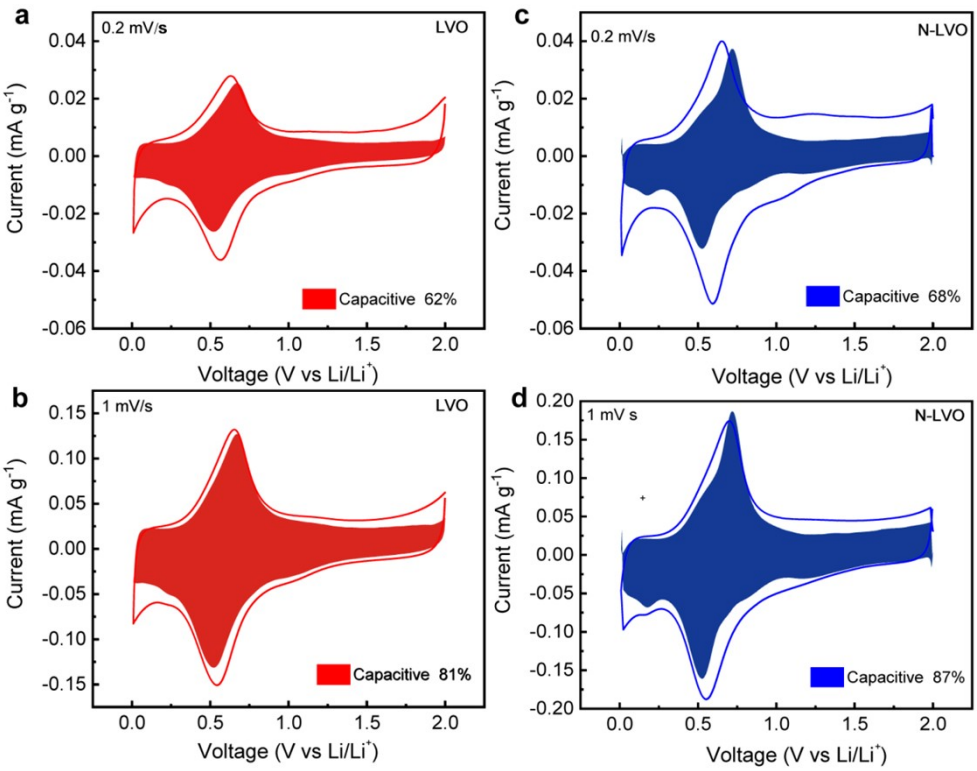


Fig. S10 CV curves of the LVO electrode at scan rates of (a) 0.2 mV s^{-1} and (b) 1 mV s^{-1} with shade region representing capacitive capacity contribution. CV curves of the N-LVO electrode at scan rates of (c) 0.2 mV s^{-1} and (d) 1 mV s^{-1} with shade region representing capacitive capacity contribution.

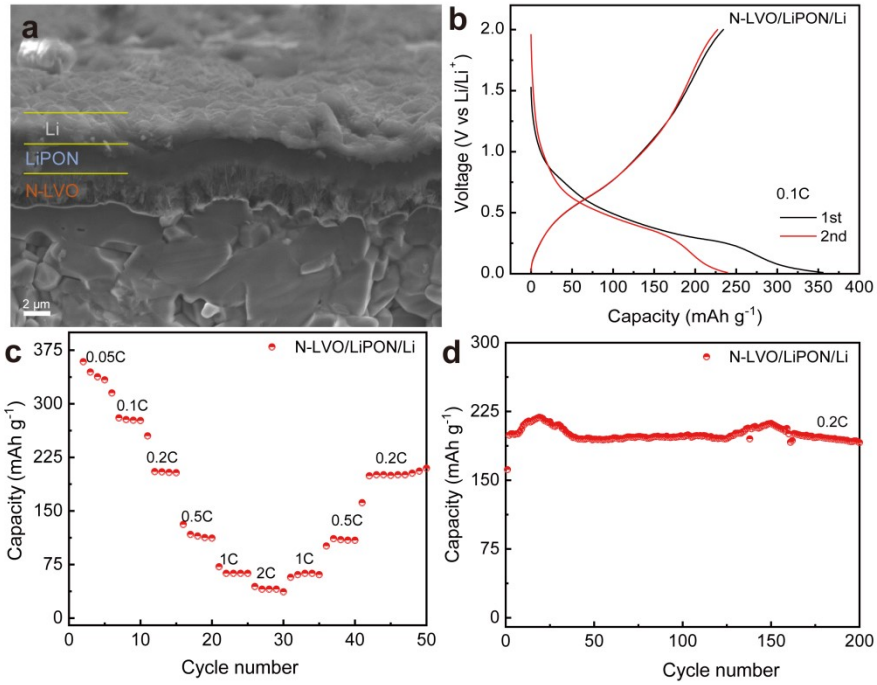


Fig. S11 (a) Cross-sectional FESEM image, (b) initial two charge and discharge curves at 0.1C, (c) rate performance, and (d) cycle performance at 0.2C of the N-LVO TFB.

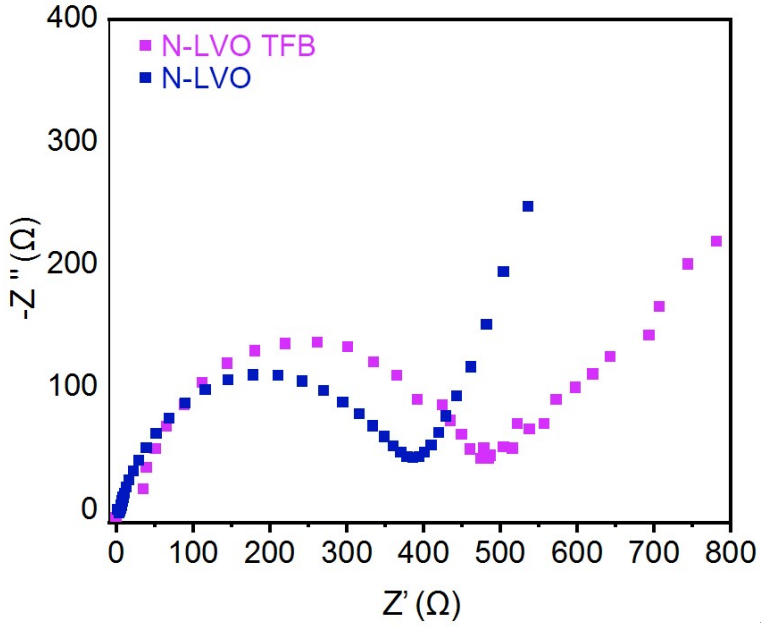


Fig. S12. Comparison of the EIS spectra of the N-LVO TFB and the N-LVO electrode.

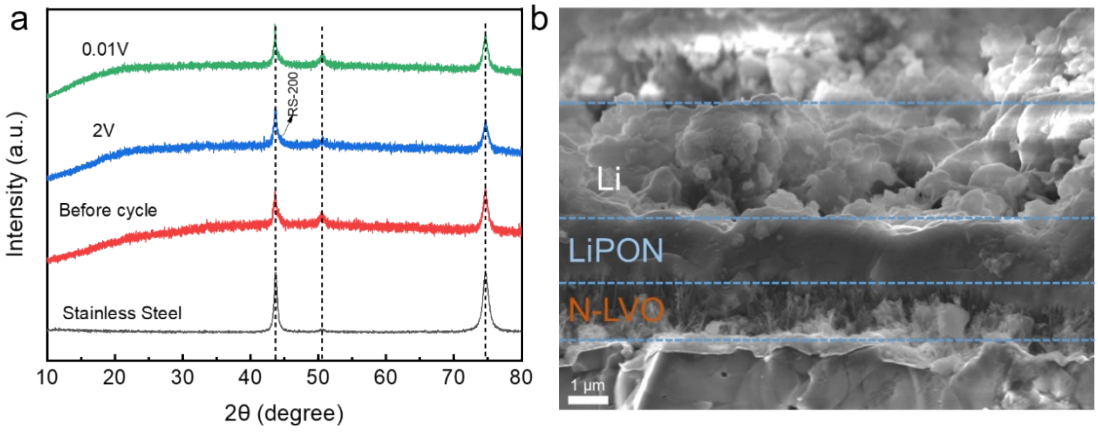


Fig. S13. (a) XRD patterns of the N-LVO TFB before cycle and at 2 V and 0.01 V states after 200 cycle. (b) Cross-sectional FESEM image of the N-LVO TFB after 200 cycles. (For the XRD measurement, the Li anode in the N-LVO TFB was pre-removed by using ethanol.)

Table. S1 Comparisons of the N-LVO anode with previously reported LVO anodes.

Samples	Specific capacity (mAh g^{-1})	Voltage range (V)	Rate performance	Cycle number/current density/ capacity retention	Ref.
Zn-$Li_3V_2O_5$ nanopowder	300 at 500 mA g^{-1}	0.01~2	155 mAh g^{-1} at 2 A g^{-1}	1000 cycles at 0.5A g^{-1} 93.34%	1
ω-$Li_3V_2O_5$ nanosheet	250 at 0.5A g^{-1}	0.01~2	113 mAh g^{-1} at 10 A g^{-1}	1000 cycles at 0.5A g^{-1} 96.8%	2
V_2O_5 nanoribbons	320 at 0.1C	/	/	1500 cycles at 1C, 78%	3
K-γ-LiV_2O_5 powder	233 at 1 A g^{-1}	0.01~3	74 mAh g^{-1} at 3 A g^{-1}	2400 cycles at 1A g^{-1}, 155.33%	4
ω-$Li_3V_2O_5$ nanosheet	250 at 1 A g^{-1}	0.01~2	153 mAh g^{-1} at 10 A g^{-1}	10000 cycles at 5A g^{-1}, 98.2%	5
$Li_3V_2O_5$ nanospheres	175 at 10 A g^{-1}	0.01~2	131 mAh g^{-1} at 20 A g^{-1}	6000 cycles at 10A g^{-1}85%	6
$Li_3V_2O_5$ nanosheet	210 at 1C	0.01~2	160 mAh g^{-1} at 5C	1000 cycles at 10C, 92.93%	7
$Li_3V_2O_5$ nanosheet	200 at 2 A g^{-1}	0.1~2	120.5 mAh g^{-1} at 20 A g^{-1}	1000 cycles at 2A g^{-1}, 95.83%	8
ω-$Li_3V_2O_5$ nanosheet	210 2 A g^{-1}	0.01~2	161.3 mAh g^{-1} at 10 A g^{-1}	1000 cycles at 1A g^{-1}, 99.13%	9
N-LVO nanosheet arrays	**350.1 at 0.1C**	**0.01~2**	**160.7 mAh g^{-1} at 10C**	**2000 cycles at 2C, 80%**	**This Work**

Table. S2 Total energy comparison of six structures predicted for N-LVO

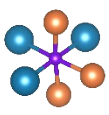
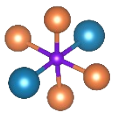
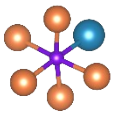
N-doped site	Initial model	3Li-3V	4Li-2V	2Li-4V	6Li	5Li-1V
Structural diagram	-					
Total energy（eV）	-1163.32	-1164.07	-1163.79	-1161.04	-1161.04	-1163.04

Table. S3 A comparison of the crystal structure information of N-LVO and LVO after

model optimization.

LVO				N-LVO			
a=8.07347, b=8.08936, c=20.74413, α=90.4402, β=90.2842, γ=901.1354				a=8.07350, b=8.089766, c=0.74410, α=90.4402, β=90.2842, γ=901.1354			
Atom	x	y	z	Atom	x	y	z
Li1	0.741642	0.738408	0.70055	Li1	0.735029	0.738391	0.699684
Li2	0.002721	0.747743	0.801643	Li2	0.002748	0.746981	0.801127
Li3	0.750763	0.744819	0.500729	Li3	0.755144	0.746668	0.499588
Li4	0.741451	0.99511	0.599741	Li4	0.744174	0.998644	0.60036
Li5	0.736304	0.510042	0.806606	Li5	0.73648	0.510065	0.806387
Li6	0.266067	0.748001	0.701443	Li6	0.272518	0.747983	0.700206
Li7	0.266421	0.991215	0.793987	Li7	0.266479	0.99113	0.793655
Li8	0.502484	0.750206	0.809653	Li8	0.502288	0.750071	0.809018
Li9	0.764503	0.748473	0.309281	Li9	0.764343	0.74881	0.309484
Li10	0.751026	0.989201	0.399897	Li10	0.749354	0.987296	0.400653
Li11	0.735115	0.49628	0.598159	Li11	0.73335	0.497144	0.598719
Li12	0.017158	0.740756	0.395946	Li12	0.018405	0.741097	0.395919
Li13	0.006501	0.240258	0.599879	Li13	0.006553	0.24112	0.600002
Li14	0.249423	0.733479	0.500033	Li14	0.245374	0.732973	0.499564
Li15	0.261449	0.012515	0.599333	Li15	0.258676	0.014318	0.600542
Li16	0.272011	0.244867	0.698971	Li16	0.272539	0.244046	0.699189
Li17	0.490505	0.995559	0.696259	Li17	0.491298	0.988031	0.695478
Li18	0.497644	0.248986	0.809179	Li18	0.497616	0.249124	0.809262
Li19	0.729456	0.730377	0.089173	Li19	0.728285	0.730545	0.089141
Li20	0.747252	0.247597	0.304779	Li20	0.746944	0.247679	0.30519
Li21	0.247597	0.749147	0.3075	Li21	0.249051	0.749032	0.307977
Li22	0.25543	0.994605	0.399506	Li22	0.25699	0.992228	0.3997
Li23	0.264	0.247473	0.500553	Li23	0.264531	0.24845	0.500882
Li24	0.498435	0.239697	0.597233	Li24	0.497622	0.242594	0.597567
Li25	0.505753	0.500606	0.70013	Li25	0.506332	0.508654	0.699298
Li26	0.723697	0.729465	0.896534	Li26	0.723323	0.729249	0.89633
Li27	0.720077	0.005235	0.980579	Li27	0.71994	0.004838	0.980095
Li28	0.992238	0.246603	0.21149	Li28	0.992567	0.24693	0.211565
Li29	0.012029	0.499853	0.305739	Li29	0.012789	0.500292	0.305781
Li30	0.237314	0.034568	0.207953	Li30	0.238121	0.034097	0.207873
Li31	0.249139	0.260484	0.298798	Li31	0.250141	0.26007	0.2988
Li32	0.253561	0.497792	0.40191	Li32	0.253576	0.498373	0.401855
Li33	0.483705	0.247872	0.40164	Li33	0.484979	0.246115	0.402111
Li34	0.487118	0.484623	0.499053	Li34	0.487076	0.483484	0.500268
Li35	0.722971	0.275225	0.891923	Li35	0.722962	0.275047	0.891999
Li36	0.728975	0.502553	0.984515	Li36	0.728712	0.502771	0.98441
Li37	0.000881	0.998265	0.893533	Li37	0.000899	0.99811	0.893006
Li38	0.988251	0.275588	0.984947	Li38	0.988343	0.274774	0.984785
Li39	0.276175	0.75417	0.894957	Li39	0.276023	0.754029	0.894669

Li40	0.505569	0.73701	0.986023	Li40	0.505248	0.736721	0.985768
Li41	0.480512	0.267406	0.203577	Li41	0.480847	0.26656	0.203808
Li42	0.982594	0.503852	0.890099	Li42	0.982688	0.503415	0.890047
Li43	0.276634	0.253886	0.894526	Li43	0.276428	0.2537	0.894449
Li44	0.27877	0.509909	0.988724	Li44	0.278746	0.510392	0.988521
Li45	0.499521	0.004565	0.894056	Li45	0.499558	0.004238	0.893776
Li46	0.501573	0.282472	0.986383	Li46	0.500884	0.282722	0.986366
Li47	0.509641	0.513085	0.08511	Li47	0.509234	0.513349	0.085219
Li48	0.52256	0.504028	0.906207	Li48	0.522305	0.503984	0.906046
V1	0.735294	0.983779	0.802521	V1	0.73536	0.983223	0.802255
V2	0.735813	0.24838	0.692124	V2	0.735151	0.249553	0.692706
V3	0.994035	0.755161	0.600951	V3	0.994173	0.754349	0.600792
V4	0.01628	0.982264	0.692685	V4	0.016006	0.981153	0.692703
V5	0.010464	0.246588	0.804426	V5	0.010789	0.246734	0.804124
V6	0.746008	0.2394	0.504878	V6	0.74601	0.241083	0.505082
V7	0.013942	0.984628	0.499933	V7	0.012348	0.986098	0.500176
V8	0.005281	0.497721	0.695532	V8	0.005648	0.498275	0.694689
V9	0.272464	0.512338	0.807568	V9	0.272594	0.512671	0.807512
V10	0.508936	0.74913	0.603039	V10	0.513459	0.7564	0.596154
V11	0.724305	0.994655	0.207744	V11	0.724404	0.99498	0.208507
V12	0.751576	0.496372	0.40254	V12	0.751955	0.497998	0.402285
V13	0.0194	0.740203	0.203779	V13	0.019452	0.740468	0.203715
V14	0.014317	0.004709	0.307058	V14	0.015303	0.004614	0.307192
V15	0.016763	0.230906	0.395275	V15	0.017562	0.230981	0.395446
V16	0.000355	0.49038	0.495853	V16	0.00121	0.490012	0.495892
V17	0.257618	0.482328	0.600694	V17	0.259839	0.483347	0.601906
V18	0.49264	0.760007	0.408471	V18	0.491219	0.756024	0.413267
V19	0.48983	0.985963	0.495334	V19	0.485918	0.982533	0.498359
V20	0.724834	0.243104	0.09774	V20	0.724716	0.243139	0.097445
V21	0.735764	0.491339	0.206472	V21	0.735724	0.491321	0.206634
V22	0.986461	0.740521	0.989083	V22	0.985765	0.7402	0.988942
V23	0.997164	-0.0012	0.10607	V23	0.996867	0.998028	0.10614
V24	0.241365	0.759012	0.110485	V24	0.240799	0.75888	0.11037
V25	0.511452	0.782788	0.206857	V25	0.511814	0.782881	0.20729
V26	0.498406	0.00791	0.297601	V26	0.499397	0.005571	0.297707
V27	0.011287	0.494553	0.108475	V27	0.010877	0.49423	0.108352
V28	0.250449	0.010197	0.993856	V28	0.249725	0.009696	0.99367
V29	0.231934	0.284252	0.103804	V29	0.231708	0.284167	0.103698
V30	0.227438	0.518407	0.19838	V30	0.227557	0.518297	0.198238
V31	0.5126	0.01697	0.105558	V31	0.511934	0.016725	0.105059
V32	0.495232	0.492026	0.301948	V32	0.495171	0.492028	0.30183
O1	0.002559	0.005326	0.790007	O1	0.002609	0.005275	0.789925
O2	0.004199	0.248215	0.887191	O2	0.003979	0.248135	0.886989
O3	0.24314	0.006013	0.912502	O3	0.242822	0.005727	0.912396

O4	0.006061	0.996278	0.596823	O4	0.005863	0.996485	0.597043
O5	0.996989	0.245382	0.69701	O5	0.996733	0.246254	0.696978
O6	0.017361	0.487252	0.789582	O6	0.018144	0.487113	0.789194
O7	0.013464	0.751788	0.907934	O7	0.012739	0.75162	0.907828
O8	0.235335	0.997533	0.696204	O8	0.234737	0.997373	0.696308
O9	0.242357	0.264278	0.793958	O9	0.242451	0.263623	0.794058
O10	0.247089	0.501087	0.88978	O10	0.246624	0.501052	0.889807
O11	0.521418	0.999698	0.792443	O11	0.521607	-0.00045	0.792329
O12	0.499707	0.239123	0.899407	O12	0.499593	0.238725	0.89953
O13	0.760694	0.00676	0.884911	O13	0.760757	0.006637	0.884642
O14	0.002263	0.988598	0.402962	O14	0.002377	0.989051	0.403059
O15	0.997182	0.237449	0.497584	O15	0.997022	0.238102	0.497813
O16	0.004349	0.501833	0.596545	O16	0.003522	0.501749	0.596298
O17	0.000973	0.744972	0.696975	O17	0.000277	0.74453	0.696786
O18	0.254452	0.991779	0.498137	O18	0.254869	0.993706	0.49936
O19	0.252761	0.263405	0.598593	O19	0.251135	0.264248	0.599014
O20	0.248054	0.497466	0.694446	O20	0.248928	0.496958	0.694754
O21	0.24753	0.729212	0.796821	O21	0.247756	0.729161	0.79668
O22	0.499091	0.983505	0.591333	O22	0.49827	0.990451	0.593139
O23	0.520948	0.242652	0.694363	O23	0.521749	0.24214	0.694739
O24	0.48353	0.497598	0.794821	O24	0.483419	0.497325	0.794894
O25	0.499029	0.770358	0.899128	O25	0.498804	0.770096	0.898909
O26	0.772144	0.007369	0.696848	O26	0.772751	0.00806	0.696987
O27	0.766559	0.232513	0.786978	O27	0.766649	0.233157	0.786912
O28	0.760865	0.500764	0.895444	O28	0.760803	0.50068	0.895378
O29	0.989188	0.99286	0.206626	O29	0.989501	0.993101	0.206737
O30	0.997299	0.244954	0.30405	O30	0.99775	0.244975	0.304255
O31	-0.00079	0.490674	0.400323	O31	0.99983	0.490534	0.40039
O32	0.998591	0.738663	0.502426	O32	0.998956	0.73907	0.50229
O33	0.251228	0.006574	0.302501	O33	0.25196	0.006034	0.302761
O34	0.23163	0.247612	0.401742	O34	0.232147	0.247161	0.401976
O35	0.236703	0.490882	0.503889	O35	0.23598	0.489646	0.504268
O36	0.24758	0.734258	0.598655	O36	0.243449	0.733148	0.598106
O37	0.502711	0.99705	0.397134	O37	0.502474	0.991098	0.3992
O38	0.508258	0.23163	0.498245	O38	0.510517	0.231753	0.498663
O39	0.490048	0.507225	0.596707	O39	0.487428	0.503724	0.597465
O40	0.50434	0.751258	0.687629	O40	0.504083	0.749967	0.684445
O41	0.752026	0.998962	0.4987	O41	0.753495	0.001659	0.499366
O42	0.75002	0.245792	0.5975	O42	0.750829	0.247463	0.597625
O43	0.764885	0.481991	0.69654	O43	0.764467	0.482493	0.696645
O44	0.758894	0.769095	0.793762	O44	0.758643	0.768867	0.79345
O45	0.01113	0.985329	0.009481	O45	0.010658	0.984818	0.00952
O46	0.988522	0.250379	0.108741	O46	0.988399	0.250032	0.10864
O47	0.982335	0.495543	0.206909	O47	0.982483	0.495802	0.206764

O48	0.005394	0.759113	0.297927	O48	0.005873	0.759261	0.297844
O49	0.246826	0.010588	0.107712	O49	0.246499	0.010449	0.107641
O50	0.238588	0.272822	0.196877	O50	0.238811	0.27269	0.196762
O51	0.257939	0.504892	0.294792	O51	0.258336	0.50454	0.294547
O52	0.273007	0.743886	0.401686	O52	0.271254	0.742776	0.401681
O53	0.47979	0.026856	0.202132	O53	0.479906	0.026519	0.202232
O54	0.497094	0.252437	0.30249	O54	0.497623	0.251318	0.303254
O55	0.50403	0.501133	0.398833	O55	0.503916	0.501265	0.398603
O56	0.501021	0.74226	0.501506	O56	0.751819	0.001722	0.301577
O57	0.751517	0.001766	0.301074	O57	0.768957	0.250035	0.406513
O58	0.768902	0.248369	0.406176	O58	0.752361	0.487871	0.497508
O59	0.751383	0.48719	0.497953	O59	0.751472	0.748785	0.597422
O60	0.750947	0.745881	0.599015	O60	0.006686	0.522365	0.011358
O61	0.007592	0.522662	0.011424	O61	0.988142	0.745513	0.105683
O62	0.988684	0.746021	0.105782	O62	0.231229	0.238929	0.013956
O63	0.23159	0.239211	0.014065	O63	0.263051	0.520324	0.101313
O64	0.263514	0.520201	0.101504	O64	0.263828	0.767851	0.206949
O65	0.26353	0.767934	0.207221	O65	0.480792	0.003758	0.016924
O66	0.481134	0.004136	0.017129	O66	0.487428	0.258085	0.106047
O67	0.48747	0.25835	0.106151	O67	0.491961	0.520393	0.205179
O68	0.491693	0.521383	0.20541	O68	0.505074	0.752231	0.302057
O69	0.50416	0.753318	0.303434	O69	0.751482	0.996395	0.108753
O70	0.75195	0.995824	0.108276	O70	0.740226	0.243909	0.20031
O71	0.74044	0.243751	0.200274	O71	0.742495	0.49624	0.305248
O72	0.742002	0.496484	0.305059	O72	0.734489	0.736494	0.402527
O73	0.732167	0.737757	0.402804	O73	0.229343	0.773316	0.013948
O74	0.229851	0.773679	0.014139	O74	0.502706	0.511334	0.999688
O75	0.502757	0.511385	0.999667	O75	0.49281	0.769906	0.112103
O76	0.493207	0.769683	0.112067	O76	0.751765	0.23965	0.015299
O77	0.752094	0.239742	0.015505	O77	0.753237	0.48665	0.111136
O78	0.753431	0.48696	0.110974	O78	0.75303	0.750412	0.205968
O79	0.752885	0.750096	0.20598	O79	0.77368	0.766629	0.999448
O80	0.774379	0.766578	-0.0005	N1	0.501644	0.742101	0.501946

Table. S4 Comparisons of the N-LVO TFB with previously reported anode materials

tested in TFBs.

Configuration	Preparation temperature	Capacity (voltage range, current rate)	Average operating voltage	Rate performance	Cycle performance	Ref.
AC-TiO_2/LiPON/Li	Room temperature	204 mAh g^{-1} (1-3 V, 50 mA g^{-1})	~1.7 V	73 mA g^{-1} at 1600 mA g^{-1}	400 cycles	10
$LiNbO_3$/LiPON/Li	Room temperature	~6.7 μAh cm^{-2} (2-5 V, 5 μA cm^{-2})	~1.2 V	/	/	11
Li_2O–Sn/LiPON/Li	300℃	~420 mAh g^{-1} (0-1 V, /)	~0.3 V	/	100 cycles	12
$Li_4Ti_5O_{12}$/LiPON/Li	230℃	~2.7 μAh cm^{-2} (1-2 V, 1C)	~1.6 V	~1.5 μAh cm^{-2} at 5C	30 cycles	13
$Li_4Ti_5O_{12}$/LiPON/Li	400℃	~33 μAh cm^{-2} (1-2 V, 3.5 μA cm^{-2})	~1.6 V	~36 μAh cm^{-2} at 35 μA cm^{-2}	10 cycles	14
$Li_4Ti_5O_{12}$/LiPON/Li	/	~1.31 μAh cm^{-2} (1-3 V, 1C)	~1.6 V	~0.2 μAh cm^{-2} at 100C	100 cycles	15
N-LVO/LiPON/Li	**Room temperature**	**315.2 mAh g^{-1} 37.8 μAh cm^{-2}** (0.01-2 V, 0.05C)	**~0.6 V**	**207 mAh g^{-1} at 0.2C**	**200 cycles**	**This work**

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