

Supporting Information

Strategy for Enhancement of Magnesium Ions Diffusion in Vanadium Tetra Sulfide-Layered Structure for Rechargeable Magnesium Batteries

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S-1: Chemicals and Materials

The reagents and chemicals were of analytical grade and were used without prior treatment or purification. Ammonium metavanadate (NH_4VO_3) purchased from Meryer Co. Ltd., Thioacetamide (TAA) and nickel acetate tetrahydrate (as Ni source) were bought from Shanghai Aladdin Bio-Chem Technology Co. Ltd and ethylene glycol (EG) were taken from Sinopharm Chemical Reagent Co. Ltd.

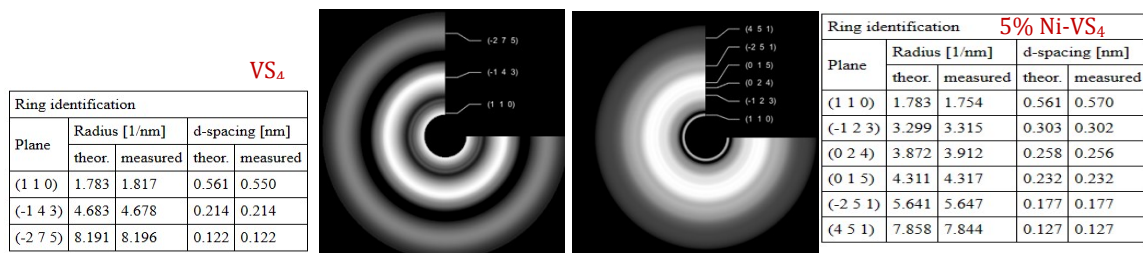
S-2: Preparation of the VS_4 Electrode - The synthesized VS_4 sample, conductive carbon black (Super P), and polyvinylidene fluoride (PVDF) with mass ratio of 7:2:1, respectively were mixed and grinding for a certain time, the powder was dissolved using solvent N-methyl-2-pyrrolidone (NMP) to obtain the slurry. The slurry was then coated onto the copper current collector that had been cut into discs thereafter in diameter 11mm and dried at 80°C for 12h.

S-3: Coin Cell Assembly - Gloves box was used for assembly of the coin type batteries for electrochemical measurements. The counter electrode selected was a high-purity Magnesium foil (99.995%, about 0.2 mm thick), it was washed in mild hydrochloric acid to remove oxide layer and surface activation. Glass fibers (Whatman, GF/D grade) were chosen as the separator

to prevent short circuit. Phenolate-based magnesium complex (PMC) electrolyte, 0.25mol/L (R-PhOMgCl)₂-AlCl₃/ THF) solution, where R is the alkyl group of 2-tert-butyl-4-methylphenol, were used as electrolyte in coin cells due to its reported high efficiency.

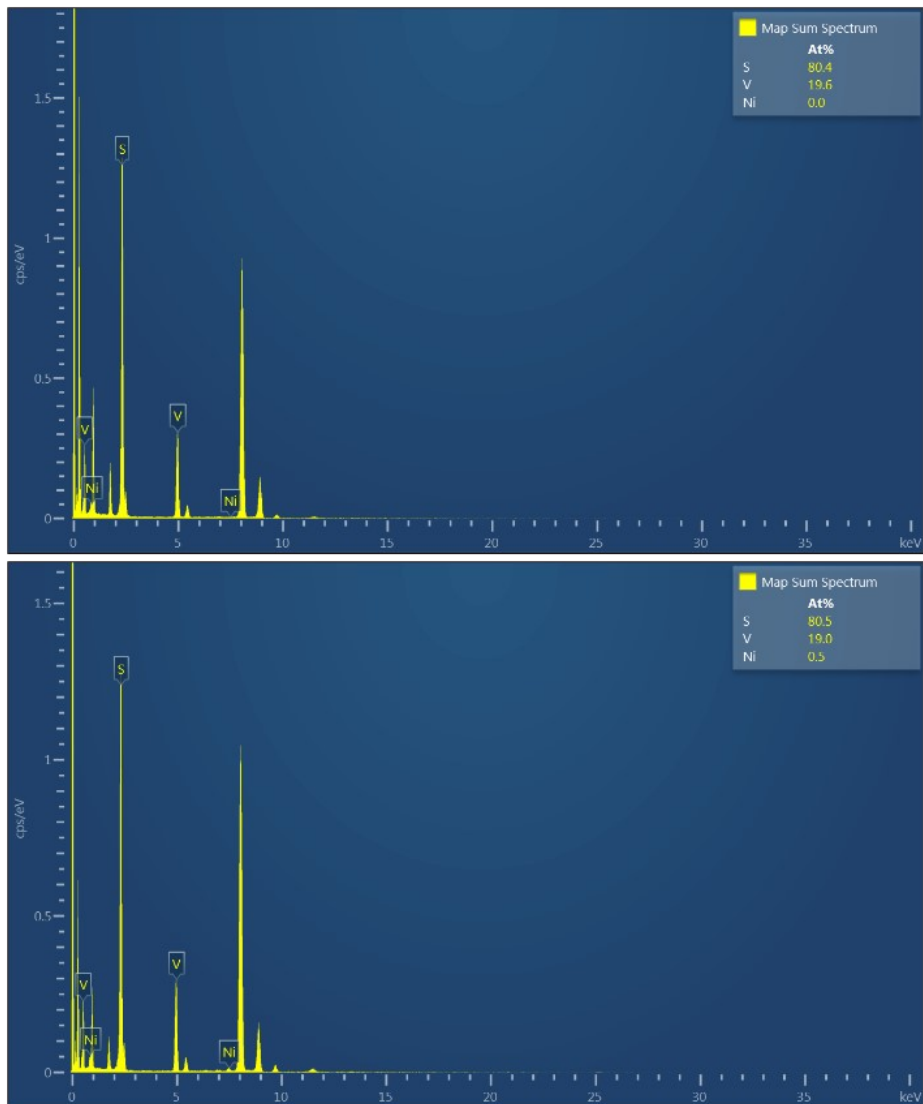
S-4: Preparation of Electrolyte - PMC electrolyte prepared in a glovebox filled with argon (both O and OH contents were maintained less than 0.01 ppm) at ambient temperature. Initially, 0.1333g anhydrous AlCl₃ (99.99% from Alfa Aesar) was dissolved in 2mL anhydrous tetrahydrofuran (THF, 99.99% from TCI) followed by stirring for 12h at 500rpm to obtain 0.5 mol/L AlCl₃/THF solution. In the meantime, 0.3284g 2-tert-butyl-4-methylphenol (99.9 % from Alfa Aesar) was added to 1mL anhydrous THF followed by stirring for 2h at 500rpm. The prepared solution is denoted as R-PhOH/THF where R represents the group of 2-tert-butyl-4-methylphenol. Then, 1mL ethyl magnesium chloride solution (2 mol/L from Aladdin) was added dropwise to the R-PhOH/THF solution, the dropwise addition is due to safety because it produces a lot of bubbles and releasing heat. Subsequently, the obtained solution was stirred for another 10h at 500rpm to obtain R-PhOMgCl/THF solution. Finally, 2.0mL AlCl₃/THF solution was mixed with 2.0mL R-PhOMgCl/THF solution to make 0.25mol/L (R-PhOMgCl)₂-AlCl₃/THF solution, which is the PMC electrolyte used in these coin cells.[1]

S-5: SAED Analysis



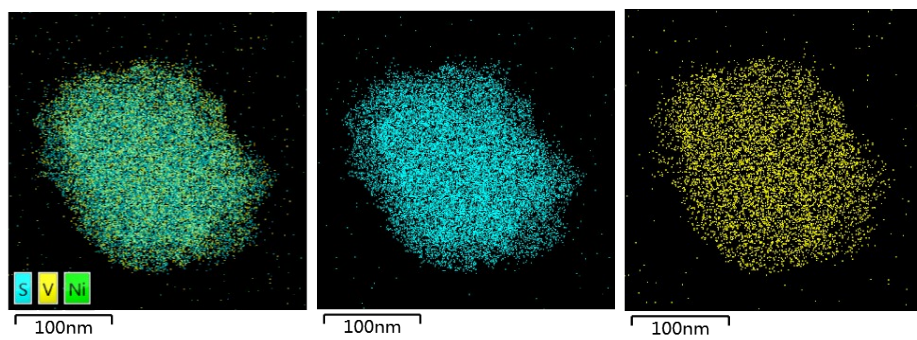
SAED image and table is showing that d spacing has been increased after nickel substitution. it was 0.550nm at 110 plane of VS₄, which was increased to 0.57nm after substitution of 5% Ni contents.

S-6: EDS Mapping



Elemental Mapping of VS₄

Dispersion of all elements are uniformly distributed. There is no Ni in pure VS₄



S-7: Table 1 Calculated sulfur (S) contents in typical metal sulfides and theoretical specific capacities based on full conversion reactions.

Cathodes for RMBS	Sulfur Contents (% wt.)	Full Conversion Reaction	Theoretical Specific Capacity (TSC), mAh/g
S	100	$Mg + S \leftrightarrow MgS$	1675
VS₄	71.6	$Mg + VS_4 \leftrightarrow MgS + 4V$	1199
FeS₂	53.4	$Mg + FeS_2 \leftrightarrow 2MgS + Fe$	894
CoS₂	52.1	$Mg + CoS_2 \leftrightarrow 2MgS + Co$	873
NiS₂	52.2	$Mg + NiS_2 \leftrightarrow 2MgS + Ni$	874
CuS	33.5	$Mg + CuS \leftrightarrow MgS + Cu$	561
Cu₂S	20.1	$Mg + Cu_2S \leftrightarrow MgS + 2Cu$	336

This table is based on hypothetical full conversion reactions-based calculation of capacitance, which shows VS₄ an Ideal candidate. However practically it could be an ideal condition only.

S-8: Table 2 Cell vectors (*a*, *b*, and *c*) in Å and atomic positions in fractional coordinates for VS₄ computed with PBE

	<i>x</i>	<i>y</i>	<i>c</i>
<i>a</i>	16.16479	0.000414	0.040128
<i>b</i>	-2.29844	16.00055	-0.04013
<i>c</i>	-1.91365	1.65836	6.900307
V	0.308097	0.441988	0.117446
V	0.308097	0.941988	0.117446
V	0.808097	0.441988	0.117446
V	0.808097	0.941988	0.117446
V	0.191903	0.058012	0.882554
V	0.191903	0.558012	0.882554
V	0.691903	0.058012	0.882554

V	0.691903	0.558012	0.882554
V	0.441988	0.308097	0.382554
V	0.441988	0.808097	0.382554
V	0.941988	0.308097	0.382554
V	0.941988	0.808097	0.382554
V	0.058012	0.191903	0.617446
V	0.058012	0.691903	0.617446
V	0.558012	0.191903	0.617446
V	0.558012	0.691903	0.617446
S	0.086249	0.343082	0.539942
S	0.086249	0.843082	0.539942
S	0.586249	0.343082	0.539942
S	0.586249	0.843082	0.539942
S	0.495497	0.202279	0.280952
S	0.495497	0.702279	0.280952
S	0.995497	0.202279	0.280952
S	0.995497	0.702279	0.280952
S	0.413751	0.156918	0.460058
S	0.413751	0.656918	0.460058
S	0.913751	0.156918	0.460058
S	0.913751	0.656918	0.460058
S	0.202279	0.495497	0.219048
S	0.202279	0.995497	0.219048
S	0.702279	0.495497	0.219048
S	0.702279	0.995497	0.219048
S	0.158169	0.186576	0.941554
S	0.158169	0.686576	0.941554
S	0.658169	0.186576	0.941554
S	0.658169	0.686576	0.941554
S	0.399552	0.445683	0.426822
S	0.399552	0.945683	0.426822
S	0.899552	0.445683	0.426822
S	0.899552	0.945683	0.426822
S	0.054317	0.100448	0.926822
S	0.054317	0.600448	0.926822
S	0.554317	0.100448	0.926822
S	0.554317	0.600448	0.926822
S	0.297721	0.004503	0.780952
S	0.297721	0.504503	0.780952
S	0.797721	0.004503	0.780952
S	0.797721	0.504503	0.780952
S	0.004503	0.297721	0.719048
S	0.004503	0.797721	0.719048
S	0.504503	0.297721	0.719048
S	0.504503	0.797721	0.719048
S	0.313424	0.341831	0.441554
S	0.313424	0.841831	0.441554
S	0.813424	0.341831	0.441554
S	0.813424	0.841831	0.441554

S	0.100448	0.054317	0.573178
S	0.100448	0.554317	0.573178
S	0.600448	0.054317	0.573178
S	0.600448	0.554317	0.573178
S	0.445683	0.399552	0.073178
S	0.445683	0.899552	0.073178
S	0.945683	0.399552	0.073178
S	0.945683	0.899552	0.073178
S	0.341831	0.313424	0.058446
S	0.341831	0.813424	0.058446
S	0.841831	0.313424	0.058446
S	0.841831	0.813424	0.058446
S	0.156918	0.413751	0.039942
S	0.156918	0.913751	0.039942
S	0.656918	0.413751	0.039942
S	0.656918	0.913751	0.039942
S	0.186576	0.158169	0.558446
S	0.186576	0.658169	0.558446
S	0.686576	0.158169	0.558446
S	0.686576	0.658169	0.558446
S	0.343082	0.086249	0.960058
S	0.343082	0.586249	0.960058
S	0.843082	0.086249	0.960058
S	0.843082	0.586249	0.960058

S-9: Table 3 Cell vectors (a , b , and c) in \AA and atomic positions in fractional coordinates for

VS_4 computed with PBE

	x	y	c
a	15.94954	0.751412	-0.07151
b	-1.52528	16.26632	-0.70548
c	-1.82345	1.2862	6.715258
V	0.313499	0.440565	0.098141
V	0.305336	0.938706	0.116781
V	0.808978	0.441273	0.11342
V	0.805552	0.944436	0.115183
V	0.190131	0.056323	0.882674
V	0.195525	0.558151	0.88773
V	0.694545	0.061581	0.869726
V	0.694657	0.559068	0.87761
V	0.44375	0.307771	0.373737
V	0.44187	0.806546	0.379564
V	0.942754	0.308673	0.379881
V	0.938653	0.807912	0.388255
V	0.056787	0.191071	0.61834
V	0.055847	0.690868	0.627629
V	0.557079	0.192029	0.617978
V	0.560249	0.691886	0.614556
S	0.091965	0.331387	0.518603

S	0.088274	0.830774	0.517362
S	0.583968	0.324923	0.512184
S	0.590817	0.833005	0.512
S	0.465408	0.174144	0.296277
S	0.483695	0.686004	0.279036
S	0.982374	0.186294	0.282108
S	0.976449	0.683875	0.295308
S	0.407637	0.174605	0.521423
S	0.411667	0.664932	0.48146
S	0.907576	0.16871	0.479256
S	0.905712	0.668107	0.500881
S	0.222676	0.508343	0.242144
S	0.205801	0.009509	0.229097
S	0.705589	0.509079	0.220154
S	0.702461	0.020249	0.213867
S	0.164853	0.190877	0.941255
S	0.171315	0.693706	0.942827
S	0.673091	0.200652	0.915693
S	0.667547	0.693004	0.938475
S	0.42416	0.452425	0.384994
S	0.405679	0.95092	0.419736
S	0.906508	0.452573	0.420941
S	0.906077	0.955004	0.419846
S	0.05678	0.120927	0.939859
S	0.064944	0.62317	0.958214
S	0.549693	0.177514	0.944517
S	0.560038	0.621876	0.93463
S	0.289149	0.985095	0.770226
S	0.291318	0.488806	0.759671
S	0.794616	0.990719	0.769668
S	0.796583	0.489852	0.76926
S	0.017841	0.313529	0.717006
S	0.017182	0.814489	0.722359
S	0.518335	0.813182	0.713796
S	0.369464	0.364089	0.556065
S	0.319504	0.858929	0.456604
S	0.819081	0.360924	0.450359
S	0.816629	0.8662	0.45653
S	0.089721	0.045743	0.57843
S	0.088779	0.544774	0.592756
S	0.587738	0.045402	0.593613
S	0.597736	0.548723	0.570151
S	0.434336	0.362871	0.031687
S	0.438836	0.875891	0.056236
S	0.94528	0.37946	0.061733
S	0.937272	0.874502	0.062677
S	0.322224	0.304492	0.066689
S	0.332279	0.804199	0.060214
S	0.837531	0.308226	0.052387

S	0.827958	0.807051	0.066303
S	0.162547	0.427839	0.059473
S	0.152632	0.925988	0.048898
S	0.656053	0.427059	0.033738
S	0.652873	0.934172	0.037738
S	0.177914	0.135965	0.543352
S	0.174222	0.635637	0.54276
S	0.672309	0.136015	0.523841
S	0.684227	0.641247	0.541699
S	0.34262	0.068508	0.950579
S	0.347658	0.572893	0.936643
S	0.847841	0.073902	0.950668
S	0.847245	0.572458	0.953793

S-10: Table 4 Cell vectors (a , b , and c) in Å and atomic positions in fractional coordinates for

Ni:VS_4 computed with PBE

	x	y	c
a	16.14472	0	0
b	-2.10279	16.0072	0
c	-1.80678	1.584954	6.877967
V	0.308049	0.441969	0.117499
V	0.308049	0.941969	0.117499
V	0.808049	0.441969	0.117499
V	0.808049	0.941969	0.117499
V	0.191951	0.058031	0.882501
V	0.191951	0.558031	0.882501
V	0.691951	0.058031	0.882501
V	0.691951	0.558031	0.882501
V	0.441969	0.808049	0.382501
V	0.941969	0.308049	0.382501
V	0.941969	0.808049	0.382501
V	0.058031	0.191951	0.617499
V	0.058031	0.691951	0.617499
V	0.558031	0.191951	0.617499
V	0.558031	0.691951	0.617499
V	0.08565	0.342714	0.540307
S	0.08565	0.842714	0.540307
S	0.58565	0.342714	0.540307
S	0.58565	0.842714	0.540307
S	0.496445	0.201743	0.27957
S	0.496445	0.701743	0.27957
S	0.996445	0.201743	0.27957
S	0.996445	0.701743	0.27957
S	0.41435	0.157286	0.459693
S	0.41435	0.657286	0.459693
S	0.91435	0.157286	0.459693
S	0.91435	0.657286	0.459693
S	0.201743	0.496445	0.22043

S	0.201743	0.996445	0.22043
S	0.701743	0.496445	0.22043
S	0.701743	0.996445	0.22043
S	0.157259	0.187011	0.942534
S	0.157259	0.687011	0.942534
S	0.657259	0.187011	0.942534
S	0.657259	0.687011	0.942534
S	0.398659	0.446	0.42802
S	0.398659	0.946	0.42802
S	0.898659	0.446	0.42802
S	0.898659	0.946	0.42802
S	0.054	0.101341	0.92802
S	0.054	0.601341	0.92802
S	0.554	0.101341	0.92802
S	0.554	0.601341	0.92802
S	0.298257	0.003555	0.77957
S	0.298257	0.503555	0.77957
S	0.798257	0.003555	0.77957
S	0.798257	0.503555	0.77957
S	0.003555	0.298257	0.72043
S	0.003555	0.798257	0.72043
S	0.503555	0.298257	0.72043
S	0.503555	0.798257	0.72043
S	0.312989	0.342741	0.442534
S	0.312989	0.842741	0.442534
S	0.812989	0.342741	0.442534
S	0.812989	0.842741	0.442534
S	0.101341	0.054	0.57198
S	0.101341	0.554	0.57198
S	0.601341	0.054	0.57198
S	0.601341	0.554	0.57198
S	0.446	0.398659	0.07198
S	0.446	0.898659	0.07198
S	0.946	0.398659	0.07198
S	0.946	0.898659	0.07198
S	0.342741	0.312989	0.057466
S	0.342741	0.812989	0.057466
S	0.842741	0.312989	0.057466
S	0.842741	0.812989	0.057466
S	0.157286	0.41435	0.040307
S	0.157286	0.91435	0.040307
S	0.657286	0.41435	0.040307
S	0.657286	0.91435	0.040307
S	0.187011	0.157259	0.557466
S	0.187011	0.657259	0.557466
S	0.687011	0.157259	0.557466
S	0.687011	0.657259	0.557466
S	0.342714	0.08565	0.959693
S	0.342714	0.58565	0.959693

S	0.842714	0.08565	0.959693
S	0.842714	0.58565	0.959693
Ni	0.441969	0.308049	0.382501

S-11: Table 5 Cell vectors (a , b , and c) in Å and atomic positions in fractional coordinates for

$\text{Ni-V}_8\text{VS}_4$ computed with PBE

	x	y	c
a	16.3299	0.686925	0.569497
b	-1.44217	15.86756	-0.03641
c	-1.51499	1.521082	6.840019
V	0.304973	0.44261	0.072274
V	0.305772	0.942988	0.122552
V	0.804574	0.440719	0.113376
V	0.811095	0.936845	0.13455
V	0.193154	0.060506	0.881278
V	0.189728	0.559041	0.864308
V	0.690733	0.057433	0.890599
V	0.688652	0.555251	0.876418
V	0.437291	0.805982	0.38646
V	0.939999	0.307395	0.379897
V	0.939077	0.806368	0.386791
V	0.061117	0.195641	0.612943
V	0.058569	0.68894	0.6174
V	0.570399	0.177123	0.646514
V	0.554892	0.690234	0.615609
V	0.067845	0.348072	0.553396
S	0.069629	0.841811	0.560684
S	0.597098	0.331458	0.580025
S	0.565699	0.842397	0.565006
S	0.49885	0.2121	0.322597
S	0.511903	0.709684	0.271375
S	0.017363	0.211999	0.268579
S	0.012365	0.707763	0.273931
S	0.439042	0.125503	0.504907
S	0.426601	0.653691	0.437865
S	0.933447	0.154844	0.438266
S	0.928085	0.653302	0.444618
S	0.185785	0.472484	0.191895
S	0.17823	0.980193	0.202497
S	0.678503	0.476665	0.199104
S	0.685808	0.975961	0.216465
S	0.134469	0.179842	0.958695
S	0.134054	0.674671	0.959988
S	0.637352	0.17544	0.983479
S	0.62985	0.673096	0.958462
S	0.367625	0.937479	0.451711
S	0.868224	0.437855	0.440135
S	0.874011	0.9357	0.456347

S	0.045678	0.092543	0.89901
S	0.044496	0.587226	0.90423
S	0.54966	0.085051	0.934382
S	0.541039	0.585392	0.901955
S	0.319928	0.022067	0.803263
S	0.318252	0.530219	0.768256
S	0.818558	0.016337	0.81191
S	0.815405	0.519636	0.78993
S	0.983737	0.291465	0.722951
S	0.985062	0.787348	0.730392
S	0.49419	0.29351	0.702805
S	0.480075	0.786539	0.731051
S	0.365001	0.42355	0.395668
S	0.299218	0.829436	0.426254
S	0.801454	0.328931	0.422272
S	0.803687	0.82787	0.442323
S	0.134626	0.067803	0.54995
S	0.125369	0.560868	0.540859
S	0.631091	0.053942	0.567027
S	0.624575	0.559768	0.549044
S	0.441255	0.396257	0.074228
S	0.453023	0.909681	0.100887
S	0.952279	0.409595	0.089301
S	0.955919	0.906841	0.097905
S	0.342545	0.325108	0.971004
S	0.363135	0.823457	0.042266
S	0.863851	0.320853	0.037862
S	0.865248	0.819654	0.047559
S	0.165214	0.40937	0.971158
S	0.167509	0.911494	0.992004
S	0.665655	0.406197	0.991821
S	0.670158	0.905928	0.009203
S	0.201045	0.175991	0.576961
S	0.192591	0.669941	0.559531
S	0.702422	0.160922	0.584405
S	0.692277	0.667865	0.570248
S	0.331577	0.09181	0.011419
S	0.327882	0.595122	0.984435
S	0.832469	0.087655	0.016538
S	0.827303	0.589885	0.997469
Ni	0.462557	0.339869	0.383301

References

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