Supporting Information

Ni-doped Magnesium manganese oxide as a cathode and its application in aqueous magnesium-ion battery with high rate performance

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Supporting Information consists of two tables and six figures over ten pages, which are Figure S1 about XRD patterns, Figure S2 about TG, Figure S3 about the Rietveld refinement, Figure S4 about the EIS measurements, 100 cycle performance and rate performances, Table S1 about the EIS values, Figure S5 about XRD patterns of original and reduced samples, Figure S6 about the XRD pattern and XPS spectra of VO_2 electrode, and the Table S2 about the comparison.



Figure S1 The XRD patterns of Ni doped Na-birnessite and Ni doped Mg-buserite, which were in accordance with the PDF cards of 43-1456 and 32-1128, respectively.



Figure S2 The TG curves of Ni_{0.1}-Mg-1, Ni_{0.3}-Mg-1, and Ni_{0.5}-Mg-1. The molecular formula of them were Ni_{0.13}MgMn₆O₁₂•3.2H₂O, Ni_{0.43}MgMn₆O₁₂•7.5H₂O, and Ni_{0.69}MgMn₆O₁₂•5.6H₂O, which were obtained by TG curve and the results of 28.98: 91.072: 1253.48, 94.56:90.783:1215.42, and 156.34: 93.15: 1266.73 (ppb) of Ni:Mg:Mn.

Intensity (a. u.)		Rwp = 0.1425	× Observe Calcula Differ Expecter ; <i>Rp</i> = 0.1022; <i>Rexp</i>	ed Data ated Pattern ence Curve ed Reflection p = 0.0263; G	Position oF = 5.42	03	
	10 20	30 40	50 60 70 20	80 90	100 11	0 120	
_cell_length_a	9.574712						
_cell_length_b	2.848142						
_cell_length_c	9.616802						
_cell_angle_alpha	90						
_cell_angle_beta	100.0275						
_cell_angle_gamn	90						
_cell_volume	258.245						
_symmetry_space	P2/m						
	_atom_sit	_atom_site_sy		atom site f	_atom_si	_atom_si	atom_site_
_atom_site_label	e_type_sy	mmetry_multi	_atom_site_fract_x	ract_y	te_fract_	te_occup	B_iso_or_e
	mbol	plicity		-	Z	ancy	quiv
Mn1	Mn	1	0.5	0.5	0	0.9954	11.95223
NI1	NI	1	0.5	0.5	0	0.0046	11.95223
Mn2	Mn	2	0.77414	0	-0.01	0.9828	11.95223
NI2	NI	2	0.77414	0	-0.01	0.0172	11.95223
Mn3	Mn	1	0	0	0.5	0.9791	11.95223
NI3	NI	1	0	0	0.5	0.0209	11.95223
MIN4	Min	2	0.98236	0.5	0.76007	0.82358	11.95223
NI4	NI	2	0.98236	0.5	0.76007	0.1/642	11.95223
01	0	2	0.12109	0.5	0.07536	1	16.51893
02	0	2	0.43004	0	0.09615	1	16.51893
03	0	2	0.69092	0.5	0.09/18	1	16.51893
04	0	2	0.96168	0	0.108/1	1	16.51893
05	0	2	0.89907	0.5	0.39805	1	16 51000
U6	0	2	0.8863	0	0.64281	1	10.51893
Wati	0	2	0.53/19	0	0.38036	1	18.//651
wat2	0	2	0.59127	0.5	0.31951	0.99724	18.77651
vvat3	0	2	0.5/8/6	0.5	0.70319	1	18.77651
Mg1	Mg	1	0.5	0.5	0.5	0.5	18.77651

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Figure S3 The Rietveld refinement results of the $Ni_{0.3}$ -Mg-1 sample. The Ni replaced the site of partial Mn and Ni and Mn were mixed located in the same sites, which indicates that Ni was indeed doped into the crystal lattice of this material successfully.



Figure S4 EIS measurements (a) and 100 cycle performance (b) of $Ni_{0.1}$ -Mg-1, $Ni_{0.3}$ -Mg-1, $Ni_{0.5}$ -Mg-1, $Ni_{0.0}$ -Mg-1 electrodes in 0.5 mol dm⁻³ Mg(NO₃)₂ electrolyte, and the rate performance of $Ni_{0.0}$ -Mg-1 and $Ni_{0.3}$ -Mg-1 two electrodes in three electrolytes (c and d). We can observe that Rs resistances of three samples decrease gradually as the increase amount of nickel doping and the Rct resistance of $Ni_{0.3}$ -Mg-1 is the minimum. The $Ni_{0.3}$ -Mg-1 electrode shows the best cycle performance, which is because the lower amount of nickel doping can not play the role of increasing conductivity and larger one hinder the insertion/deinsertion of magnesium ion. Therefore, the appropriate amount of nickel doping can be beneficial for $Ni_{0.3}$ -Mg-1 electrode to exhibit more excellent electrochemical performance.

solutions	$0.5 mol \cdot dm^{-3} MgCl_2$	$0.5 \text{mol} \cdot \text{dm}^{-3} \text{Mg}(\text{NO}_3)_2$	$0.5 mol \cdot dm^{-3} MgSO_4$
$R_{\rm s}(\Omega) \pm 0.001$	3.597	5.128	8.223
CPE-T±0.01 E-5	2.218E-4	2.094E-4	3.445E-4
CPE-P±0.0001	0.78771	0.8141	0.7238
$R_{\rm ct}(\Omega) \pm 0.001$	4.440	3.735	12.76
σ±0.01	19.97	16.16	23.28
$D_{\rm Mg}^{2+}({\rm cm}^2~{\rm s}^{-1})\pm 0.01{\rm E}\text{-}15$	3.43E-16	5.12E-16	2.51E-16

Table S1 Evaluated impedance parameters, σ and ${D_{\rm Mg}}^{2+}$ values in the different

electrolytes



Figure S5 The XRD patterns of original and reduced Ni_{0.3}-Mg-1 electrodes. We can observe that the peak at 2θ =9.46° of original electrode shift to the lower angle after the discharge process, which was the peak at 2θ =9.33°. It proved that the magnesium ions have inserted into the lattice of host material.



Figure S6 The XRD patterns of different charged/discharged VO₂ electrodes (a), XPS patterns of reduced electrode at first cycle (b), oxidized sample at first cycle (c) and reduced electrode at 30^{th} cycle. It can be found that the original VO₂ electrode changed to be a stable new material of MgVO_x after first reduced state, which was composed of Mg_{0.01}V₂O₅ (JCPDS:89-0610), V₅O₉ (JCPDS:80-2027) and the unknown phase. After the first charged process, the MgVO_x electrode with stable structure is more beneficial for magnesium ions insertion/deinsertion. In 10th cycle, 20th cycle and 30th cycle, the XRD peaks of electrode was becoming increasingly amorphous and widened. Many peaks were getting harder to observe but the peaks of new formative phase at 2θ =20.4°, 22.3° and original VO₂ peaks at 2θ =25.4° and 30.4° can be still observed, which indicated that the new formative phase after first reduced

process was very stable. Fig. S6b shows that the existence of more magnesium ions was observed in the survey spectra of reduced VO₂ electrodes. In the Fig.S6c and d, a part of V⁴⁺ oxidized to V⁵⁺ during the discharged state, and after 30th cycle, the wide peak located at 516.5 eV is analyzed and V⁴⁺ and V³⁺ for reduced sample are obtained by fitting the datum, which together which further proves that stable MgVO_x was formed after first charged process and MgVO_x as the anode will achieve the insertion/deinsertion of magnesium ions accompanied by the changes of V⁴⁺ reduced to V³⁺ and V⁴⁺ oxidized to V⁵⁺.

Cathode/anode	Electrolyte	current density/ mA g ⁻¹	Capacity/mAh g ⁻¹
Prussian Blue/Polyimide[s1]	MgSO ₄	200	35.0
MgxMo ₃ S ₄ /Mg[s2]	Mg(AlCl ₂ BuEt) ₂ /THF	200	75.0
$TiSe_2/Mg[s3]$	Mg(AlCl ₂ BuEt) ₂ /THF	1 C	108
$Mo_6S_8/Mg[4]$	Mg(BH ₄) ₂ /LiBH ₄ /DGM	C/10	99.5
LiMn ₂ O ₄ /LiTi ₂ (PO ₄) ₃ [s5]	Li_2SO_4	4mA/cm^{-2}	40
NaMnO ₂ /NaTi ₂ (PO ₄) ₃ [s6]	Na_2SO_4	1 C	33
Our work	MgSO ₄	200	102.7

Table S2 The compared condition on some different magnesium ion battery systems.

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