Supporting Information

Inert V₂O₃ Oxide Promotes the Electrocatalytic Activity of Ni Metal for Alkaline

Hydrogen Evolution

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Experimental Section

Materials: Ammonium metavanadate (NH₄VO₃), oxalic acid (H₂C₂O₄·2HO), nickel chloride (NiCl₂·6H₂O), potassium hydroxide (KOH) and sulfuric acid (H₂SO₄) were purchased from Chengdu Kelong Chemical Reagent Factory (China). Pt/C (20 wt.% Pt on Vulcan XC-72R) and Nafion (5 wt.%) were purchased from Sigma-Aldrich. All chemical reagents used in this experiment were of analytical grade. The water used throughout all experiments was purified through a Millipore system.

Preparation of $Ni_xV_{1-x}O_2$ network on Ti plate ($Ni_xV_{1-x}O_2$): 1.0 mmol NH₄VO₃ and 1.2 mmol H₂C₂O₄·2H₂O were added into a mixed solution (25 mL H₂O and 10 mL ethanol) to form a uniform yellow solution. After magnetic stirring for 30 min, 0.25 mmol NiCl₂·6H₂O was added into the aboved solution and keep stirring for 10 min. Then the obtained solutions were transferred into 40 mL Teflon-lined stainless steel autoclave with titanium foil which was pretreated in 3 M HCl for 30min and washed with distilled water (DW) and ethanol. The autoclaves were maintained at 180°C for 2 h, and then cooled to room temperature naturally. The obtained samples were washed with DW for several time and dried in vacuum at 60°C.

Preparation of Ni/V_2O_3 *on Ti plate (Ni/V_2O_3):* The aboved $Ni_xV_{1-x}O_2$ were heated at 5°C min⁻¹ up to 550°C for 2 h in a reducing atmosphere composed of 10% H₂ and 90% N_2 (100 sccm/min), and then cooled to room temperature in a tube furnace. The preparation of samples with different temperatures were the same as the above-mentioned process but changed the carbonization temperature. The catalyst loading of

Ni/V₂O₃ on the Ti plate is 0.6 mg/cm². The sample named Ni/V₂O₃@400 means it reduced at 400 °C, and Ni/V₂O₃ means sample reduced at 550 °C unless stated otherwise. *Preparation of Pt/C electrode*: The commercial 20 wt.% Pt/C samples were prepared by ultrasonically mixing 4 mg of the catalyst powder with the mixture of 40 μ L 5% Nafion solution, 560 μ L ethanol and 400 μ L H₂O for 15 min to form homogeneous catalyst ink. Next, a certain volume of the ink was carefully dropped onto the clean carbon paper, leading to a desirable catalyst loading of about 1.0 mg cm⁻².

General characterizations: The surface morphology and the microstructure of the catalysts were analyzed by X-ray diffraction (XRD-6000, Shimadzu), X-ray photoelectron spectroscopy (XPS, PHI 550 ESCA/SAM), field-emission scanning electron microscopy (FE-SEM, JSM-7800, Japan), and energy dispersive X-ray spectra (EDS, OXFORD Link-ISIS-300), respectively. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscope (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV.

Electrochemical measurements: Electrochemical measurements were performed in a three-electrode cell system with a CHI660D electrochemical analyzer (CH Instruments, Inc., Shanghai). Sizable and shapeable electrodes can be prepared by simply tailoring the Ti foil, and the obtained Ni/V₂O₃ can be directly used as the working electrode (1 cm²) without employing extra substrates (e.g., glassy-carbon electrode) or binders (e.g., Nafion). To avoid the deposition of Pt, a carbon rod in parallel orientation to the working electrode was used as the counter electrode with a distance of 1 cm and an Hg/HgO electrode was used as the reference electrode. The electrolyte (1.0 M KOH)

was degassed by bubbling N_2 for at least 30 minutes before the electrochemical measurements. Linear sweep voltammetry (LSV) was performed in N_2 saturated aqueous solution with a scan rate of 10 mV s⁻¹ in a range from 0 to -0.6 V. Durability test was carried out by cyclic voltammetry (CV) from -0.6 V to 0 vs. RHE for 1000 at a scan rate of 50 mV s⁻¹ and i-t curve at current density of 10 mA/cm² for over 20 h. In all measurements, the potentials reported in our work were vs. a reversible hydrogen electrode (RHE). All currents presented were corrected against ohmic potential drop. The electrochemical surface area (ECSA) of these catalysts were estimated by cyclic voltammetry. CV was performed in the potential range without a redox process from 0.2 to 0.3 V (vs RHE) at varying rates from 5 to 35 mV s⁻¹ in 1.0 M KOH. The electrochemical impedance spectroscopy (EIS) measurements were carried out from 100000 to 0.1 Hz in in 1.0 M KOH at the potential of -0.2 V vs. RHE.



Figure S1. (a) LR- and (b) HR-TEM images of Ni/V₂O₃. SEM images of (c) V₂O₃ and (d) Ni.



Figure S2. EDX of of Ni/V₂O₃.



Figure S3. XRD patterns of Ni/V₂O₃ reduced at different temperatures.



Figure S4. (a) Ni 2p, (b) V 2p and (c) O 1s XPS spectra of Ni/V_2O_3 reduced at different temperatures.



Figure S5. (a) Estimation of C_{dl} by plotting the current density variation ($\Delta j = (j_a - j_c)/2$); CVs of (b) Ni, (c) V₂O₃ and (c)Ni/V₂O₃ with various scan rates (5-35 mV/s) in the region of 0.25 to 0.35 V vs RHE.



Figure S6. (a) Polarization curves, (b) Tafel plots, (c) Nyquist plots and (d) Estimation of C_{dl} of Ni/V₂O₃ reduced at different temperatures.



Figure S7. CVs of (a) $Ni/V_2O_3@400$, (b) $Ni/V_2O_3@500$, (c) $Ni/V_2O_3@550$, (d) $Ni/V_2O_3@600$, (e) $Ni/V_2O_3@650$ and (f) $Ni/V_2O_3@700$ with various scan rates (5-35 mV/s) in the region of 0.25 to 0.35 V vs RHE.

Catalysts	Onset potential (mV)	Tafel slope (mV dec ⁻¹)	Overpotential @10mA/cm ² (mV)	C _{dl} (mF cm ⁻ ²)	$\mathrm{R_{s}}\left(\Omega ight)$	R _{ct} (Ω)
Ni	-141	-116	-268	2.86	1.103	22.71
V_2O_3	-100	-728	<-600	14.03	1.165	104.5
Ni/V ₂ O ₃	-30	-112	-140	17.49	0.994	9.612

Table S1. Summary of the HER performance of Ni, V_2O_3 , and Ni/ V_2O_3 reduced in 550°C.

Table S2. Summary of HER performance of Ni/V_2O_3 reduced at different temperatures.

Catalysts	Onset potential (mV)	Tafel slope (mV dec ⁻¹)	Overpotential @10mA/cm ² (mV)	C _{dl} (mF cm ⁻ ²)	$\mathrm{R}_{\mathrm{s}}\left(\Omega ight)$	R _{ct} (Ω)
Ni/V ₂ O ₃ @400	-70	-145	-191	16.44*	0.8738	26.14
Ni/V ₂ O ₃ @500	-67	-116	-172	33.62	0.8970	16.67
Ni/V ₂ O ₃ @550	-30	-112	-140	17.49	0.9938	9.612
Ni/V ₂ O ₃ @600	-71	-131	-196	18.43	0.9250	17.13
Ni/V ₂ O ₃ @650	-64	-142	-200	10.42	1.000	18.88
Ni/V ₂ O ₃ @700	-100	-151	-246	8.62	1.028	43.47

Catalysts	Mass loading (mg cm ⁻²)	media	Current density (mA/cm ²)	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	reference
Ni/V ₂ O ₃ -Ti	0.6	1 M KOH	-10	-140	-112	This work
Ni-Mo/Ni foam	-	6 M KOH	-100	-178	-	1
NiMoN	0.25	0.1 M HClO ₄	onset	-78	-36	2
NiO/Ni-CNT	0.28	1 M KOH	-10	~-100	-82	3
Ni(OH)2@Ni/CC	2.8	1 M KOH	-10	-68	-97	4
Ni ₃ S ₂ /NF	~1.6	1 M KOH	-10	-170	-	5
NiSe	0.28	0.5 M H ₂ SO ₄	-10	~-280	-64	6
HP-NiSe ₂	-	0.5 M H ₂ SO ₄	-10	-57	-43	7
Ni ₂ P	1.0	0.5 M H ₂ SO ₄	-20	-130	-46	8
Mn-Ni ₂ P/NF	7.0	1 M KOH	-20	-103	-82	9
MoS ₂ -Ni ₃ S ₂ HNRs/NF	13	1 M KOH	-10	-98	-61	10
Ni _{0.95} Co _{0.05} PS ₃	0.51	1 M KOH	-10	-71	-77	11
Ni-MoC	0.12	1 M KOH	-10	-123	-84	12

Table S3. Summary of Ni-based electrocatalysts for HER.

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