Electronic Supporting Information

Modifying Mn₃O₄ by CeO₂ for enhanced electrocatalytic water oxidation

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General materials

All chemicals were commercially available and were used without further purification. $Mn(NO_3)_2$ (AR, 50 wt.% in H₂O), Ce(NO₃)₃·6H₂O (AR, 99%), KOH (AR, 95%) and ethanol (EtOH, AR, 99.7%) were acquired from Energy Chemical Reagent Co., Ltd. Commercial carbon cloth (CC) was purchased from the Fuel Cell Store. Milli-Q water of 18.2 MΩ·cm was used in all experiments.

Synthesis of materials

Prior to the electrodeposition, the carbon cloth ($0.5 \text{ cm} \times 2 \text{ cm}$) was washed with acetone for 30 min to ensure that surface pollutants were removed, and subsequently rinsed with ethanol several times to clean it well. Then it was soaked in 2.0 M H_2SO_4 for 2 h, treated with deionized water to neutral, and dried at room temperature. Firstly, the corresponding metal hydroxide was synthesized by a simple anion-assisted cathodic co-electrodeposition method on the CC substrate. Cathodic reactions of NO³⁻ generate hydroxide ions and lead to an increase in pH value close to the CC cathode surface, thereby thermodynamically driving the deposition of metal hydroxide. The corresponding metal nitrate solution has a total concentration of 0.05 M. Then, for the synthesis of the Ce-doped metal precursors, 0.1, 0.2, 0.5, 1, 2 and 5 mol% of Mn(NO₃)₂ in the solution were substituted with Ce(NO₃)₃. The electrodeposition was performed in a typical three-electrode cell configuration, where the working electrode was the CC (0.5 cm × 0.5 cm), the reference electrode was saturated Aq/AqCl and the counter electrode was a graphite rod. Then, the constant potential of -1.0 V (vs Ag/AgCI) was applied to the CC substrate for 120, 300, and 600 s. Following electrodeposition, the metal hydroxide precursors were left to dry under room temperature for two hours. Then, they were transferred into a tubular furnace and underwent calcination in an air environment at 300 °C for 2 h. The metal hydroxide precursors were converted into corresponding oxides.

Physical characterizations

Under the accelerated voltage of 5 kV, the morphologies of samples were observed by Hitachi SU8020 high-resolution field emission SEM. TEM images of samples were captured at 200 kV on a Tecnai G2 F20 (FEI) field emission transmission electron microscope. Energy dispersive X-ray spectroscopy (EDX) data were collected on the AMETEK analysis equipped on a scanning electron microscopy. X-ray diffraction (XRD) patterns of samples were recorded on an X-ray diffractometer (Bruker, D8 Advance, Cu K α , λ = 1.5406 A, 40 kV/40 mA). The Raman spectra were obtained on a Lab RAM Odyssey spectrometer equipped with a 532 nm excitation laser. X-ray photoelectron spectroscopy (XPS) information of the sample was obtained by XPS instrument (Kratos AXIS ULTRA, AI K α , hv = 1486.6 eV, C 1s = 284.8 eV). The XAFS spectra were obtained on the laboratory easyXAFS300+ spectrometer. The XANES and EXAFS data were analyzed and fitted by ATHENA and ARTEMIS software programs.

Electrochemical studies

All oxygen evolution reaction (OER) electrochemical measurements were performed on an electrochemical workstation (CHI 660E, CH Instruments, Inc.) by a three-electrode system in 1.0 M KOH aqueous solution at 25 °C. The loaded CC with a working area of 0.5 mm × 0.5 mm is used as the working electrode, the graphite rod is used as the counter electrode and the saturated Ag/AgCl is used as the reference electrode. All potentials in this work are reported against the reversible hydrogen electrode (RHE) based on the equation: $E_{RHE} = E_{Ag/AgCl} + (0.197 + 0.0591 \times pH)$ V. Linear sweep voltammetry (LSV) was performed at 10 mV s⁻¹ with iR-compensation of 95%. The electrochemical active surface area (ECSA) of CeO₂/CC, Mn₃O₄/CC and CeO₂-Mn₃O₄/CC were evaluated by the double layer capacitance (C_{dl}), which was estimated from cyclic voltammetry (CV) at different scan rates in the non-faradaic regions. The relationship between ECSA and C_{dl} is shown in equation: ECSA = C_{dl} / C_{s} , where C_{s} is general specific capacitance, which is a constant of 0.04 mF cm⁻² in the literature.¹ The tafel plots were derived from the steady state currents. The electrochemical impedance spectroscopy (EIS) method was conducted in a frequency range of 0.1 to 100000 Hz. In addition, chronoamperometry and chronopotentiometry measurements were performed to analyse the long-term stability of the electrocatalyst in OER.



Fig. S1 (a, b) SEM images of blank CC. (c) Photographs of blank CC substrate (left), CeO₂-Mn₃O₄/CC precursor (middle) and annealed CeO₂-Mn₃O₄/CC (right).



Fig. S2 SEM images of CeO₂/CC.



Fig. S3 SEM images of Mn₃O₄/CC.



Fig. S4 EDX spectrum of CeO₂-Mn₃O₄/CC.



Fig. S5 XRD pattern of CeO₂/CC.



Fig. S6 XPS survey scan spectra of Mn_3O_4/CC and $CeO_2-Mn_3O_4/CC$.



Fig. S7 LSV curves of catalysts with varying CeO_2 incorporation amounts (0-5%) at deposition times for (a) 120 s, (b) 300 s, and (c) 600 s.



Fig. S8 Charging currents of (a) CeO_2/CC , (b) Mn_3O_4/CC and (c) $CeO_2-Mn_3O_4/CC$ composites recorded in the non-faradaic potential region at different scan rates.



Fig. S9 LSV curves of the catalysts normalized by ECSA.



Fig. S10 The staircase chronopotentiometry at different current densities of CeO₂- Mn_3O_4/CC ; inset: comparison of LSV and chronopotentiometry results.



Fig. S11 Chronoamperometry of Mn_3O_4/CC for 24 h.



Fig. S12 SEM images of (a-c) Mn_3O_4/CC and (d-f) $CeO_2-Mn_3O_4/CC$ materials after OER tests.



Fig. S13 XRD patterns of Mn₃O₄/CC and CeO₂-Mn₃O₄/CC materials after OER tests.



Fig. S14 XPS spectra of Mn₃O₄/CC and CeO₂-Mn₃O₄/CC materials after OER tests.

Different electrolyte solution concentration									
Total amount of	The content of Ce (%) and the millimole of material								
substance	containing metal ion in solution								
(5 mmol)	0	0.1	0.2	0.5	1	2	5		
Mn(NO₃)	5	4.995	4.99	4.975	4.95	4.9	4.75		
Ce(NO ₃) ₃	0	0.005	0.01	0.025	0.05	0.1	0.25		

Table S1 The calculation of the electrolyte solution concentration.

Catalysts	Electrolyte	η (mV) @10 mA/cm²	Tafel Slope (mV/dec)	Ref.
CeO ₂ -Mn ₃ O ₄ /CC	1.0 M KOH	266	92	This work
Mn ₃ O ₄	1.0 M KOH	890	343	2
N-MnO ₂ ^V	1.0 M KOH	312	89	3
LiNi0.5Mn1.5O4	1.0 M KOH	320	72	4
$Fe_{10}Co_{40}Mn_{50}O$	1.0 M KOH	310	45	5
Co ₂ MnO ₄	1.0 M KOH	328	66	6
Mo/a-MnO ₂	1.0 M KOH	440	86	7
Mn ₃ O ₄ @CS/CP	1.0 M KOH	390	98	8
Ag/Mn ₃ O ₄	1.0 M KOH	338	-	9
Al-Mn ₃ O ₄	1.0 M KOH	450	109	10
CeO₂-CuO- Mn₃O₄@rGO	1.0 M KOH	270	92	11
Mn ₁ -N ₂ S ₂ C _x	1.0 M KOH	280	44	12
Ni/MnO@N-C NS/NF	1.0 M KOH	306	91	13
Irsa-MnOx	1.0 M KOH	252	64	14
P-Gd SAs@MnO₂	1.0 M KOH	281	162	15
A-MnO ₂ /NSPC	1.0 M KOH	280	63	16
Mn-NSG	1.0 M KOH	296	38	17
PBN-Ir/Mn	1.0 M KOH	220	89	18
Mn ₃ O ₄ /O-CNTs	1.0 M KOH	410	75	19
Doped MnO ₂ /CFP	1.0 M KOH	390	104	20
Mn ₂ O ₃ :2.64%Mo	1.0 M KOH	570	75	21
FeNiMnO4/CeO2	1.0 M KOH	241	45	22
$Mn_{7.5}O_{10}Br_{3}$	0.5 M H ₂ SO ₄	295	68	23

Table S2 A comparison of the OER performance of CeO_2 -Mn₃O₄/CC and other recently developed Mn-based electrocatalysts.

Catalysts	R _s (Experiment)	R _s (Fitted)	R _{ct} (Fitted)
CeO2/CC	5.099 Ω	5.125 Ω	196.8 Ω
Mn ₃ O ₄ /CC	5.164 Ω	5.211 Ω	77.1 Ω
CeO2-Mn3O4/CC	5.521 Ω	5.587 Ω	55.8 Ω

Table S3 Experimentally measured R_s and Z-view fitted R_s and R_{ct} values of catalysts.	

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