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## **Electronic Supplementary Information**

Pt/Mn<sub>3</sub>O<sub>4</sub> cubes with high anti-poisoning ability for C1 and C2 alcohol fuel oxidation

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## **Experiments**

### Materials and chemicals

Manganese(II) sulfate tetrahydrate (MnSO<sub>4</sub>·4H<sub>2</sub>O), urea and hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) were bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Sodium borohydride (NaBH<sub>4</sub>) were purchased from Shandong Xiya Chemical Industry Co., Ltd. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion (5 wt.%) was purchased from Sigma-Aldrich. Vulcan XC-72 carbon black was purchased from the Cabot Corporation. All of the above chemical reagents were of analytical grade and used as received. All solutions were prepared with ultrapure water (Thermo Fisher Scientific (USA) Co., Ltd).

## Preparation of Mn<sub>3</sub>O<sub>4</sub> and Pt-Mn<sub>3</sub>O<sub>4</sub> catalysts

Synthesis of  $Mn_3O_4$ : It was fabricated following the procedure reported elsewhere with some modifications<sup>[1]</sup>.  $Mn(NO_3)_2.4H_2O$  (1.69 g) and urea (3.00 g) were dissolved in water (40 mL) and stirred for 20 min; the solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave followed by heating at 100 °C for 16 h in an electric oven. After cooling down naturally to room temperature, the products of  $MnCO_3$  were separated and collected by centrifugation and dried at 60 °C for 12 h.  $Mn_3O_4$  was then obtained by thermal annealing  $MnCO_3$  at 800 °C for 14 h in a flow  $N_2$  atmosphere.

Synthesis of Pt-Mn<sub>3</sub>O<sub>4</sub>: A given amount of chloroplatinic acid solution (10 mg Pt) was added into 40 mL of water, and its pH was adjusted to neutral by adding 2 M NaOH solution. Then 40 mg of Mn<sub>3</sub>O<sub>4</sub> powder was added into the above solution, and they were ultrasonicated for 10 min. Finally, an excess amount of 0.01 M NaBH<sub>4</sub> solution was added dropwise into the solution and they were kept stirring for more than 15 min at room temperature. The catalyst of Pt-Mn<sub>3</sub>O<sub>4</sub> (Pt, wt.20%) was obtained by filtration and washing with water carefully, and the obtained catalyst powder was dried at 60 °C in the oven before use.

## **Physical characterization**

The catalysts were characterized by Bruker D8 advance X-ray diffraction (XRD) with Cu K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) measurement was carried on an ECSALAB250Xi S3 spectrometer with an Al K $_{\alpha}$  radiation source. The morphology was examined

with FEI Sirion-200 scanning electron microscope (SEM) and a transmission electron microscope (TEM) operating at 200 kV. The Pt (220) peak was fitted to a Gaussian line shape on a linear background to calculate the particl size. The crystal size of Pt nanoparticles was calculated according to Scherrer formula:D=K $\lambda$ / $\beta$ cos $\theta$ , Where, D=crystallites size (nm); K=0.9 (Scherrer constant);  $\lambda$ =0.15406 nm (wavelength of the x-ray sources);  $\beta$ =FWHM (radians);  $\theta$ =Peak position (radians).

#### **Electrochemical measurements**

All electrochemical measurements were performed using a conventional three-electrode system done on a bio-logic VSP electrochemical workstation (bio-logic Co., France). The catalyst-coated glassy carbon electrode with a surface area of 0.07 cm<sup>-2</sup> was employed as the working electrode, and the current density was reported based on this geometric surface unless otherwise noted. The graphite rods and saturated calomel electrodes (SCE, Hg/Hg<sub>2</sub>Cl<sub>2</sub>) were used as the counter and reference electrodes, respectively. The catalyst ink was prepared by mixing catalyst (3 mg), carbon black (3 mg), 570  $\mu$ L of ethanol, and 30  $\mu$ L of a 5 wt. % Nafion solution under ultrasonication. 10  $\mu$ L of the catalyst ink was drop-cast to the glass carbon electrode and dried naturally before use. The Pt loading in the electrode was 0.14 mg cm<sup>-2</sup>.

Cyclic voltammetry(CV) was done for methanol or ethanol oxidation in the electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 M CH<sub>3</sub>OH or 1.0 M CH<sub>3</sub>CH<sub>2</sub>OH at a potential range between -0.2 V and 1.0 V vs. SCE at a potential scan rate of 50 mV s<sup>-1</sup>. A chronoamperometry (CA) experiment was carried out to evaluate the catalytic stability correspondingly at the fixed potentials for 7200 s. CO-stripping experiments were carried out using the same approach reported elsewhere<sup>[2]</sup>. The high purity CO (99.9%) was bubbled to the electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub> for 20 minutes when the potential was set at 0 V vs. SCE. Then the nitrogen was bubbled into the electrolyte for 15 min to remove the excess CO dissolved in the electrolyte. The potential range of CO stripping was -0.2 ~ 1.0 V vs. SCE at a potential scan rate of 20 mV s<sup>-1</sup>. The electrochemical active surface areas (ECSA) were estimated by the CO stripping test, assuming that the coulombic charge required for the CO monolayer oxidation was 420  $\mu$ C cm<sup>-2</sup>. The electrochemical impedance spectra (EIS) were recorded at the frequency range from 1000 kHz to 30 mHz. The amplitude of the sinusoidal potential signal was 5 mV. An accelerated stability test was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub>/1 M CH<sub>3</sub>OH and 0.5 M

 $\rm H_2SO_4/1~M~CH_3CH_2OH$  solution with a scanning rate of 150 mV s^-1.



**Fig. S1.** (a) XRD pattern of Pt-Mn<sub>3</sub>O<sub>4</sub> catalyst. Mn<sub>3</sub>O<sub>4</sub> phase (JCPDS Card No. 24-0734) and Pt phase (JCPDS Card No. 87-0646). (b-c) TEM images of MnCO<sub>3</sub> at different magnifications.



Fig. S2. (a-b) TEM images of  $Mn_3O_4$  at different magnifications.



Fig. S3. (a-b) TEM images of  $Pt-Mn_3O_4$  at different magnifications.



Fig. S4. High-resolution TEM image of Pt-Mn<sub>3</sub>O<sub>4</sub> catalysts.



Fig. S5. Energy-dispersive X-ray spectroscopy spectrum of  $Pt-Mn_3O_4$  catalyst.



Fig. S6. XPS spectrum of C 1s region for Pt-Mn<sub>3</sub>O<sub>4</sub> catalyst.



Fig. S7. XPS spectrum of O 1s region for Pt-Mn<sub>3</sub>O<sub>4</sub> catalyst.



Fig. S8. The equivalent circuit used in EIS fitting.

The  $R_s$  corresponds to the solution resistance, the constant phase element of CPE composition represents the double-layer capacitance,  $R_{CT}$  is for the charge transfer resistance caused by methanol oxidation, L usually refers to the external circuit inductance and does not include electrochemical process,  $R_0$  is relevant to the contact resistance between the catalyst and the glass carbon electrode.



Fig. S9. Cyclic voltammetry curves in 0.5 M  $H_2SO_4$  solution with 1 M CH<sub>3</sub>OH at different scan rates of 5, 10, 20, 50, 75, 100 and 150 mV s<sup>-1</sup> for Pt-Mn<sub>3</sub>O<sub>4</sub> catalysts (a) and Pt/C (b).



Fig. S10. Cyclic voltammetry curves in 0.5 M  $H_2SO_4$  solution with 1 M  $CH_3CH_2OH$  at different scan rates of 5, 10, 20, 50, 75, 100 and 150 mV s<sup>-1</sup> for Pt-Mn<sub>3</sub>O<sub>4</sub> catalysts (a) and Pt/C (b).



Fig. S11. Tafel plots of Pt-Mn<sub>3</sub>O<sub>4</sub> and Pt/C catalysts for methanol (a) and ethanol (b) oxidation



**Figure S12.** Cyclic voltammograms of Pt-Mn<sub>3</sub>O<sub>4</sub> (a) and Pt/C (b) catalysts for 0.5M H<sub>2</sub>SO<sub>4</sub>/1M CH<sub>3</sub>OH solution at 150 mV s<sup>-1</sup> in an accelerated stability test for 1000 cycles. Normalized peak current density versus the scanning cycles for Pt-Mn<sub>3</sub>O<sub>4</sub> and Pt/C catalyst (c).



**Figure S13.** Cyclic voltammograms of Pt-Mn<sub>3</sub>O<sub>4</sub> (a) and Pt/C (b) catalysts for  $0.5M H_2SO_4/1M CH_3CH_2OH$  solution at 150 mV s<sup>-1</sup> in an accelerated stability test for 1000 cycles. Normalized peak current density versus the scanning cycles for Pt-Mn<sub>3</sub>O<sub>4</sub> and Pt/C catalyst (c).



Fig. S14. Specific activity and mass activity of Pt-Mn<sub>3</sub>O<sub>4</sub> and Pt/C catalysts for ethanol oxidation.

Catalysts	Assignment	Binding energy / eV	Relative intensity / %
Pt-Mn <sub>3</sub> O <sub>4</sub>	<b>D</b> +0	71.2	70
	Pt°	74.6	12
	Pt <sup>2+</sup>	72.2	28
		75.7	28
	<b>D</b> 40	71.5	(5
Pt/C	Pt°	74.9	03
	$Pt^{2+}$	72.5	25
		76.0	33

Table S1. Binding energies of Pt  $4f_{7/2}$  and  $4f_{5/2}$  components for Pt-Mn<sub>3</sub>O<sub>4</sub> catalysts and Pt/C.

Catalyst	Assignment	Binding energy / eV	Relative intensity / %
	Mæ <sup>2+</sup>	640.4	19.2
	IVIn <sup>2</sup>	652.0	18.5
	Mn <sup>3+</sup>	641.8	40.2
Pt-MIn <sub>3</sub> O <sub>4</sub>		653.4	49.5
	Mn <sup>4+</sup>	643.6	22.4
		655.2	52.4

Table S2. XPS fitting of Mn 2p and its contents in  $Pt-Mn_3O_4$  catalyst.

**Table S3.** EIS fitting parameters from equivalent circuits for different catalysts in the  $0.5 \text{ M H}_2\text{SO}_4$ +1 M CH<sub>3</sub>OH solution.

Samples	$R_S/\Omega$	CPE-Yo /Ss <sup>-n</sup>	CPE-n	C/ F	$R_{CT}/\Omega$	L / H	$R_0  /  \Omega$	Chi-squared
Pt-Mn <sub>3</sub> O <sub>4</sub>	8.5	6.1 E-4	0.75	2.8 E-4	212	1.4 E-5	4.5	8.3 E-2
Pt/C	8.7	8.3 E-2	0.90	2.5 E-4	470	1.6 E-6	5.5	1.0 E-2

**Table S4.** EIS fitting parameters from equivalent circuits for different catalysts in the  $0.5 \text{ M H}_2\text{SO}_4$ +1 M CH\_3CH\_2OH solution.

Samples	$R_S/\Omega$	CPE-Yo /Ss <sup>-</sup>	CPE-n	C/ F	$R_{CT}$ / $\Omega$	L / H	$R_0  /  \Omega$	Chi-squared
Pt-Mn <sub>3</sub> O <sub>4</sub>	8	7.5 E-6	0.77	3.3 E-4	810	2.2 E-5	7.5	9.1 E-2
Pt/C	8.7	4.5 E-4	0.91	4.5E-5	1900	6.5 E-7	14	6.1 E-3

**Table S5.** Onset potential and CO oxidation peak potential for CO stripping voltammograms andthe estimated ECSA for Pt- $Mn_3O_4$  and Pt/C catalysts.

Somulas	Onset potential Oxidation peak pote		ntial $ECSA (m^2 c^{-1})$	
Samples	(V vs. SCE)	(V vs. SCE)	$LCSA(IIF g^{-})$	
Pt-Mn <sub>3</sub> O <sub>4</sub>	0.3	0.41	63.3	
Pt /C	0.48	0.57	49	

**Table S6.** Comparison of the specific activity and mass activity of Pt-Mn<sub>3</sub>O<sub>4</sub> and Pt/C catalysts in the 0.5 M  $H_2SO_4$  +1 M CH<sub>3</sub>OH solution.

Commiss	Specific activity	Mass activity
Samples	$(mA \ cm_{Pd}^{-2})$	$(mA mg_{Pd}^{-1})$
Pt-Mn <sub>3</sub> O <sub>4</sub>	2	1272.6
Pt/C	0.5	248.5

**Table S7.** Comparison of the specific activity and mass activity of  $Pt-Mn_3O_4$  and Pt/C catalysts in the 0.5 M  $H_2SO_4 + 1$  M  $CH_3CH_2OH$  solution.

Commiss	Specific activity	Mass activity
Samples	$(mA \ cm_{Pd}^{-2})$	$(mA mg_{Pd}^{-1})$
Pt-Mn <sub>3</sub> O <sub>4</sub>	1.35	852
Pt/C	0.49	239

# References

- 1. Fan, X., S. Li, and L. Lu, *Porous micrometer-sized MnO cubes as anode of lithium ion battery*. Electrochimica Acta, 2016. **200**: p. 152-160.
- 2. Bao, Y., et al., *Pd/FeP catalyst engineering via thermal annealing for improved formic acid electrochemical oxidation*. Applied Catalysis B: Environmental, 2020. **274**: p. 119106.