Supplementary Materials

Alternative aqueous phase synthesis of a PtRu/C electrocatalyst for direct methanol fuel cells

Qijun Wang [1], Ya-Wei Zhou [1], Zhao Jin [2,*], Chunguang Chen[1,3], Hong Li [1,*] and Wen-Bin Cai [1,*]

[1] Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, Shanghai 200438, China

[2] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

[3] Department of Chemistry, University of Shanghai for Science and Technology, Shanghai 200093, China

* Correspondence: zjin@ciac.ac.cn; hongli17@fudan.edu.cn; wbcai@fudan.edu.cn

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Table S1. The average particle sizes of JM Pt/C, JM PtRu/C, PtRu/C(DMAB) and PtRu/C($NaBH_4$) catalysts obtained from XRD and TEM (simply named as $\bar{d}_{XRD}$ and $\bar{d}_{TEM}$), respectively.

Catalyst	$\bar{d}_{XRD}$	$\bar{d}_{TEM}$
JM Pt/C	2.8	2.7
JM PtRu/C	2.9	2.6
PtRu/C(DMAB)	2.1	2.0
PtRu/C($NaBH_4$)	2.5	2.7

Table S2. The binding energies and relative intensities of Pt^0 $4f_{7/2}$ core level XPS spectra for JM Pt/C, JM PtRu/C, PtRu/C(DMAB) and PtRu/C($NaBH_4$) catalysts.

Catalyst	Species	Binding energy (eV)	Relative intensity (%)
JM Pt/C	Pt^0 $4f_{7/2}$	71.1	57
JM PtRu/C		71.4	57
PtRu/C(DMAB)		72.3	61
PtRu/C($NaBH_4$)		72.0	62

Table S3. The binding energies and relative intensities of Ru^0 $3p_{3/2}$ core level XPS spectra for JM PtRu/C, PtRu/C(DMAB) and PtRu/C($NaBH_4$) catalysts.

Catalyst	Species	Binding energy (eV)	Relative intensity (%)
JM PtRu/C	Ru^0 $3p_{3/2}$	462.6	65
PtRu/C(DMAB)		462.6	75
PtRu/C($NaBH_4$)		462.8	73

Table S4. The onset (E_{onset}) and peak potentials (E_{peak}) of CO stripping on JM Pt/C, JM PtRu/C, PtRu/C(DMAB) and PtRu/C($NaBH_4$) catalysts in 0.5 M H_2SO_4.

Catalysts	E_{onset} (V)	E_{peak} (V)
JM Pt/C	0.435	0.527
JM PtRu/C	0.150	0.265
PtRu/C(DMAB)	0.141	0.252
PtRu/C($NaBH_4$)	0.145	0.269

Table S5. The electro-oxidation performance on JM Pt/C, JM PtRu/C, PtRu/C(DMAB) and PtRu/C($NaBH_4$) catalysts in 0.5 M H_2SO_4 + 1 M CH_3OH at a scan rate of 50 mV/s (columns 2-4) or a constant potential of 0.25 V (column 5).

Catalyst	E_{onset} (V)	MA (A mg^{-1}_{Pt})	i_f / i_b	i_{3600} (mA mg^{-1}_{Pt})
JM Pt/C	0.210	0.36	1.07	0.8
JM PtRu/C	0.140	0.30	1.80	23.3
PtRu/C(DMAB)	0.120	0.53	1.72	35.4
PtRu/C($NaBH_4$)	0.144	0.50	1.55	31.9

Table S6. Comparison of synthetic process, particle size and MOR parameters of the PtRu/C catalysts from this work and recent publications.

Catalyst	Synthetic process	Particle size (nm)	E_{peak} of CO oxidation (V vs. SCE)	$C_{Methanol}$ (M)	Scan rate (mV/s)	MA (A/mg_{Pt})	Ref.
PtRu-CoP/C-40%	Polyol reduction	2.6	0.38	1.0	50	1.01	[1]
PtRu30/TECNF	Polyol reduction	3.5	0.33	0.5	20	0.45	[2]
PtRu/CB@NxC-20%	Organic phase synthesis	3.8	0.41	1.0	50	0.51	[3]
PtRu Nws/C	Organic phase synthesis	1.8	Not mentioned	0.5	50	0.82	[4]
PtRu/PC-H	Impregnation-H_2	2.8	0.39	0.5	50	1.67	[5]
HCNT/E-HBM/ PtRu@PBI	Polymer coating	2.2	0.38	1.0	50	0.40	[6]
Pt_1Ru_1 nano-sponge	Aqueous phase synthesis	Not particle	0.29	1.0	50	0.30	[7]
PtRu/BDDNP	Aqueous phase synthesis	4.0	0.31	1.0	50	0.29	[8]
PtRu/PPDA-MWCNTs	Aqueous phase synthesis	3.5	0.35, 0.58	1.0	50	0.73	[9]
PtRu/C(DMAB)	Aqueous phase synthesis	2.0	0.252	1.0	50	0.53	This work
JM PtRu/C	Maybe organic phase synthesis	2.7	0.265	1.0	50	0.30	This work

Table S7. IR band assignments in this work.

Wavenumber (cm^{-1})	Assignments
~ 2340	asymmetric stretching of interfacial CO_2 [10-12]
2019~2053	linearly bonded CO on Pt (Pt-CO_L) [13-15]
1935~1972	linearly bonded CO on Ru (Ru-CO_L) [16-18]
~ 1723	C=O stretching of dissolved formic acid (HCOOH) [10,13,19]
~ 1610	bending modes δ(HOH) of interfacial water [17,20,21]
~ 1323	bridge-bonded formate ($HCOO_B$) [14,22,23]

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