Electronic Supplementary Information for the manuscript

Enhancing the catalytic and electrocatalytic properties of Pt-based catalysts by forming bimetallic nanocrystals with Pd

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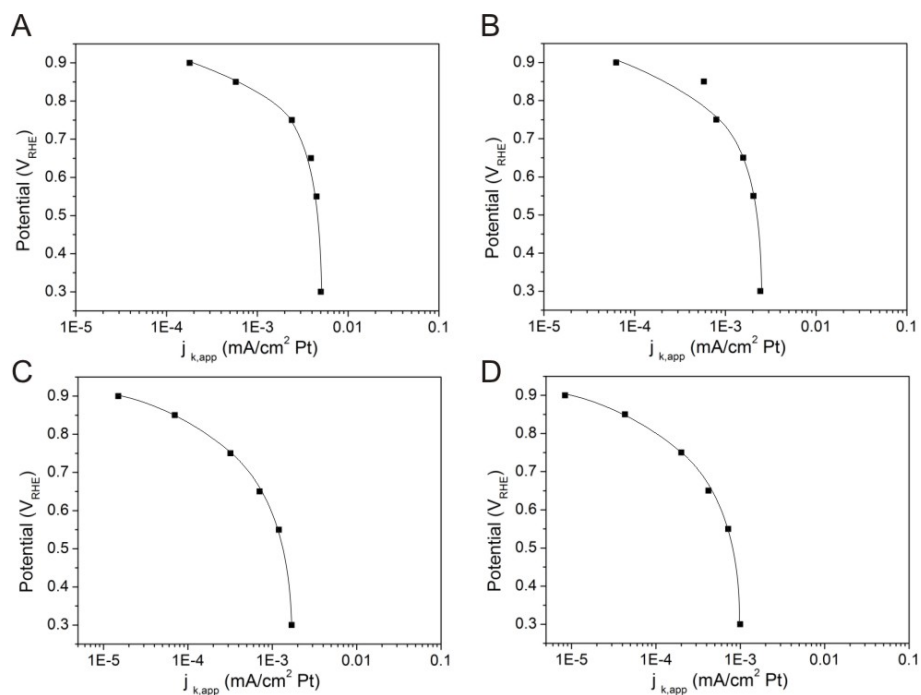*E-mail: younan.xia@bme.gatech.edu*

Fig. S1 Tafel curves for the apparent ORR kinetic currents ($j_{k,app}$) using Pd-Pt concave nanocubes as catalysts with different weight percentages of Pt: (A) 3.4, (B) 10.4, (C) 19.9, and (D) 34.3%.

In general, the Kouteck-Levich equation is applied to calculate the kinetic current density of ORR, which can be described as:[1]

$$1/j = 1/j_k + 1/j_d \qquad (1)$$

where j is the experimentally measured current density, j_d is the diffusion-limiting current density, and j_k is the kinetic current density. In a standard measurement, the diffusion-limiting current density j_d for ORR has to be within 10% of the theoretical value (5.8 mA/cm^2) derived from the following equation:[2]

$$j_d = 0.2nFD_o^{2/3}C_o\, v^{-1/6}\omega^{1/2} \qquad (2)$$

where n is the number of electrons transferred, F is the Faraday constant, D_o is the diffusion coefficient of O$_2$ gas (1.9×10^{-5} cm^2/s), v is the kinematic viscosity of water (0.01 cm^2/s), C_o is the concentration of O$_2$ gas in a dilute aqueous solution (1.1×10^{-5} mol/cm^3), and ω is the rotation rate of the electrode in unit of rpm.

In our study of ORR with Pd-Pt concave nanocubes as catalysts, the limiting current

densities were about 5.0 mA/cm^2 based on the polarization curve (Fig. 12A), which was lower than the ideal value (5.8 mA/cm^2). This was caused by the insufficient loading of metal catalysts.[3] As such, it is not proper to estimate the kinetic current density (j_k) by using the equation 1 due to the existence of internal mass transfer limitation. As such, the values of j_k in Fig. 12, that were obtained from the curves at 0.9 V versus RHE, might bear measurement errors. According to the method reported in literature,[4] we can estimate the measurement error of j_k when j_d is lower than the ideal value due to the insufficient loading of the metal catalyst. In this case, two types of mass transfer limitation existed. One is the external diffusion as described by the rotating-speed-dependent Kouteck-Levich equation. The other one is the internal diffusion within the electrode. These can be described according to the following equations:

$$1/j = 1/j_{E.D.,limiting} + 1/j_{k,app} \qquad (3)$$

$$1/j_{k,app} = 1/j_{I.D.,limiting} + 1/j_{k,true} \qquad (4)$$

where j is the experimentally measured current density, $j_{E.D.,limiting}$ is the external diffusion-limiting current density, $j_{k,app}$ is the apparent kinetic current density, $j_{I.D.,limiting}$ is the internal diffusion-limiting current density, and $j_{k,true}$ is the true kinetic current density. When $j_{E.D.,limiting}$ takes the ideal value of 5.8 mA/cm^2, equation 3 becomes equation 1. $j_{k,app}$ is the true kinetic current density. From the ORR polarization curve (Fig. 12A), we can obtain the Tafel plot (Fig. S1).[1] If the apparent kinetic currents are the true kinetic currents, they are expected to follow the Butler-Volmer equation, that is, shown as a straight line in the Tafel plot. Fig. S1 shows the apparent ORR kinetic currents ($j_{k,app}$) for the catalysts of Pd-Pt concave nanocubes with different weight percentages of Pt in the Tafel curves. All of them showed a curved line with a limiting current. It suggested that a second mass transfer limitation was involved, which can be identified as the internal mass transfer limitation. In addition, $j_{I.D.,limiting}$ was obtained by extrapolating the plots to the infinite minimum of potential according to equation 4. As a result, $j_{k,app}$ and $j_{k,true}$ were both obtained according to equations, 3 and 4 (see Table 1). Their related errors were calculated, which were smaller than 10%. Taken together, our ORR measurements were deviated from the standard condition because the limiting current density did not approach the ideal value. However, the $j_{k,true}$ can

still be obtained according to the aforementioned method.

Table 1 A summary of $j_{k,app}$, $j_{k,true}$, and their related measurement errors at 0.9 V versus RHE for catalysts with different weight percentages of Pt.

Catalysts with different weight percentages of Pt	$j_{k,app}$ (mA/cm^2)	$j_{k,true}$ (mA/cm^2)	Errors (%)
3.4%	0.000170	0.000183	7.1
10.4%	0.0000626	0.0000643	2.7
19.9%	0.0000154	0.0000156	1.3
34.3%	0.00000840	0.00000850	1.2

References

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