Supporting Information

Self-stabilized Pt-Rh bimetallic nanoclusters as durable electrocatalyst for dioxygen reduction in PEM fuel cells

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Figure S1. FESEM images of supportless nanoclusters of SL Pt_3Rh NC (a & b) and VC supported Pt_3Rh NC (c & d).



Figure S2. (a) EDX pattern, (b) SEM and elemental mappings of (c) Pt, (d) Rh for supportless Pt_3Rh nanoclusters.



Figure S3. Comparison of (a) cyclic voltammograms in N_2 and (b) linear scan voltammograms in O_2 saturated 0.5 M H₂SO₄ for SL Pt-Rh nanoclusters with different atomic wt. % compositions at 25 °C.



Figure S4. Comparison of (a) mass transfer corrected Tafel plots and (b) K-L plots of SL Pt-Rh nanoclusters with different atomic wt. % compositions in O_2 saturated 0.5 M H₂SO₄ at a scan rate of 0.01 V s⁻¹ at 25 °C.



Figure S5. Mass transfer corrected Tafel plots of supportless Pt_3Rh and Pt_3Rh/VC nanoclusters in O_2 saturated 0.5 M H_2SO_4 at 2400 rpm at a scan rate of 0.01 V s⁻¹ at 25 °C.



Figure S6. ADT (a) CVs and (b) LSVs of Pt₃Rh/VC nanoclusters and (c) comparison of normalized ECSA for both supportless and VC supported Pt₃Rh nanoclusters during potential cycling.



Figure S7. (a) TEM image, (b) EDX pattern, (c) CV in N_2 and (d) LSVs at different rotation rates in O_2 saturated 0.5 M H₂SO₄ for SL Pt@Pt₃Rh nanoclusters at 25 °C.



Figure S8. Comparison of LSVs for supportless $Pt@Pt_3Rh$ and Pt_3Rh nanoclusters at rotation rate of 2400 rpm in O₂ saturated 0.5 M H₂SO₄ nanoclusters at 25 °C.

Table S1. Comparison of ORR kinetic parameters for supportless Pt-Rh nanoclusters with different atomic weight percentage composition.

Pt-Rh (atomic wt. % composition)	<i>j_d</i> (mA cm ⁻²)	Onset Potential (V)	b (mV dec ⁻¹)	<i>E</i> _{1/2} (V)	10 ⁶ * <i>i</i> ₀ (A cm ⁻²)	n	
3:1	3.92	0.73	132	0.61	1.30	4.0	
1:1	2.96	0.68	143	0.57	0.57	2.65	
1:3	2.78	0.59	159	0.45	0.35	2.61	

 $\overline{j_d}$ -limiting current density; $E_{1/2}$ -half-wave potential; *b*-Tafel slope; α -electron transfer coefficient; i_0 -exchange current density; *n*-number of electron transfer.