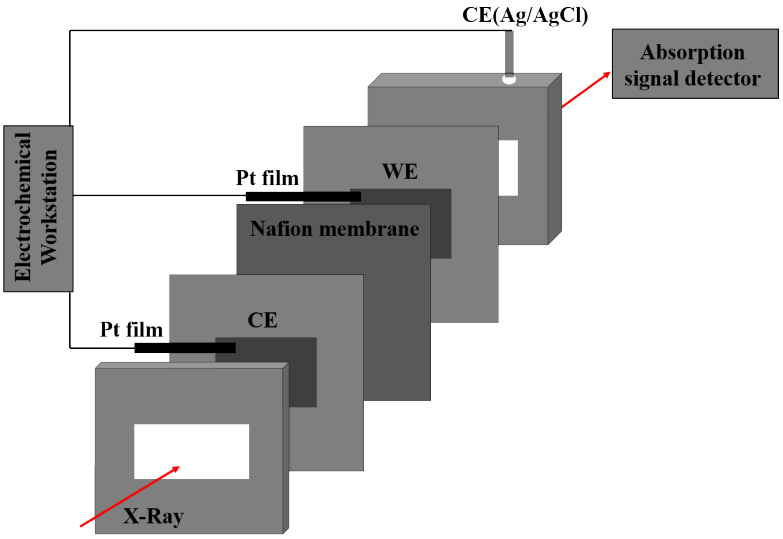
Supporting Information

Comparative investigation on the activity degradation mechanism of Pt/C and PtCo/C electrocatalysts in PEMFCs during accelerate degradation process characterized by an In-Situ X-ray absorption fine structure

FangLing Jiang[1], FengJuan Zhu[1], Fan Yang[1], XiaoHui Yan[1], AiMing Wu[1], LiuXuan Luo[1], XiaoLin Li[1], JunLiang Zhang[1,*]

1 Shanghai Jiao Tong Univ, Inst Fuel Cells, Shanghai 200240, Peoples R China

** Corresponding author. E-mail addresses: junliang.zhang@sjtu.edu.cn;*



Scheme S1. The setup of in-situ XAS measurement fuel cell. The incident X-Ray beam hits the MEAs sample, which is composed of CE, nafion membrane and WE, and creates a absorption signal at the detector. WE, CE and RE were connected with the extra electrochemical workstation through Pt film due to investigate the potential-dependence structure of the sample. RE, reference electrode; WE, working electrode; CE, counter electrode.

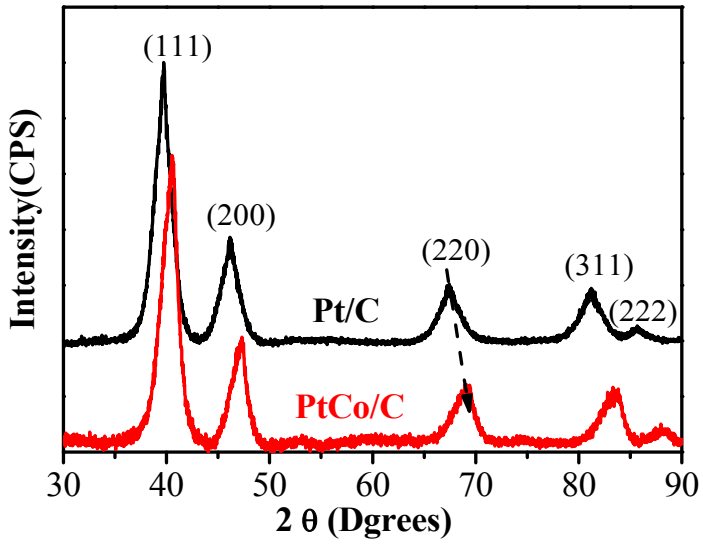


Figure S1. XRD patterns for as-prepared Pt/C and PtCo/C electrocatalysts.

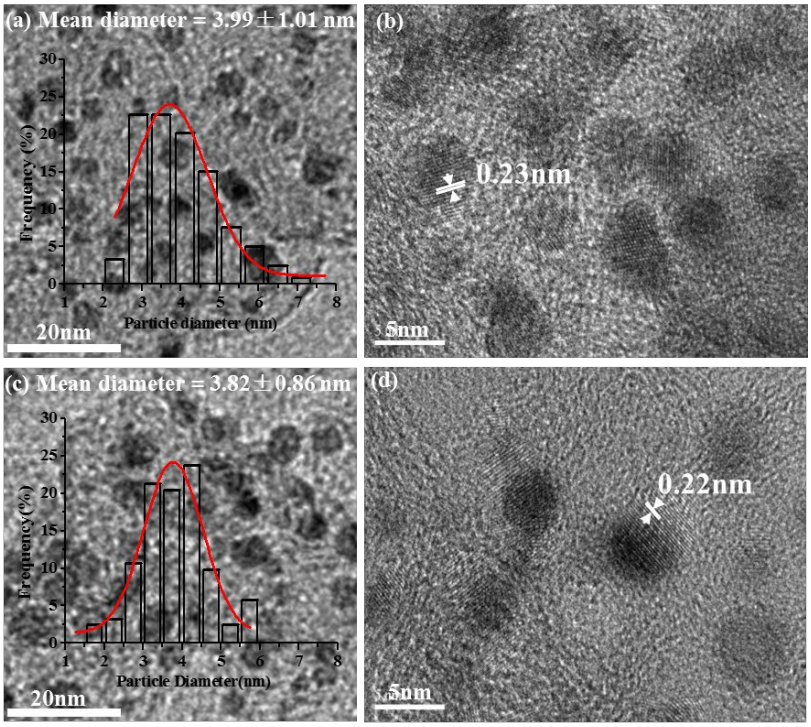


Figure S2. Representative TEM images and the corresponding histograms of particle diameter distribution (insets) for as-prepared Pt/C (a) and PtCo/C (c) electrocatalysts. The HRTEM images for as-prepared Pt/C (b) and PtCo/C (d) electrocatalysts.

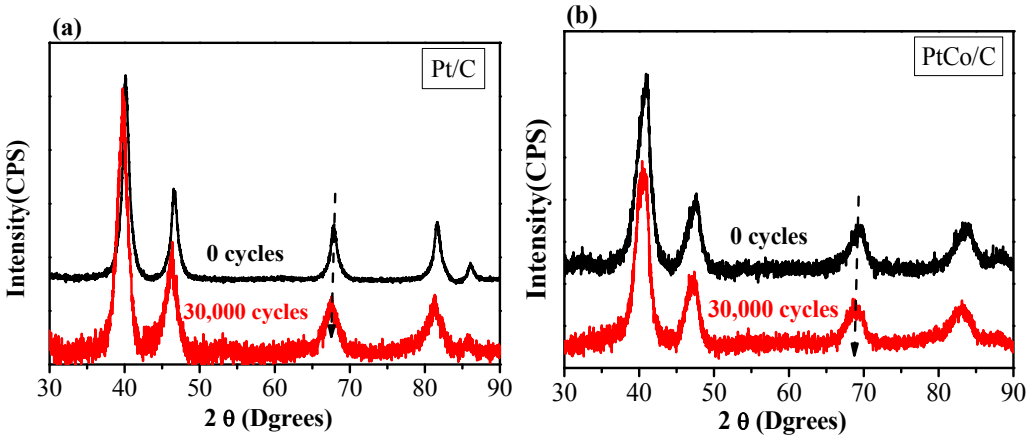


Figure S3. XRD patterns for Pt/C (a) and PtCo/C (b) electrocatalysts in MEAs at the 0 and 30,000 ADT cycles.

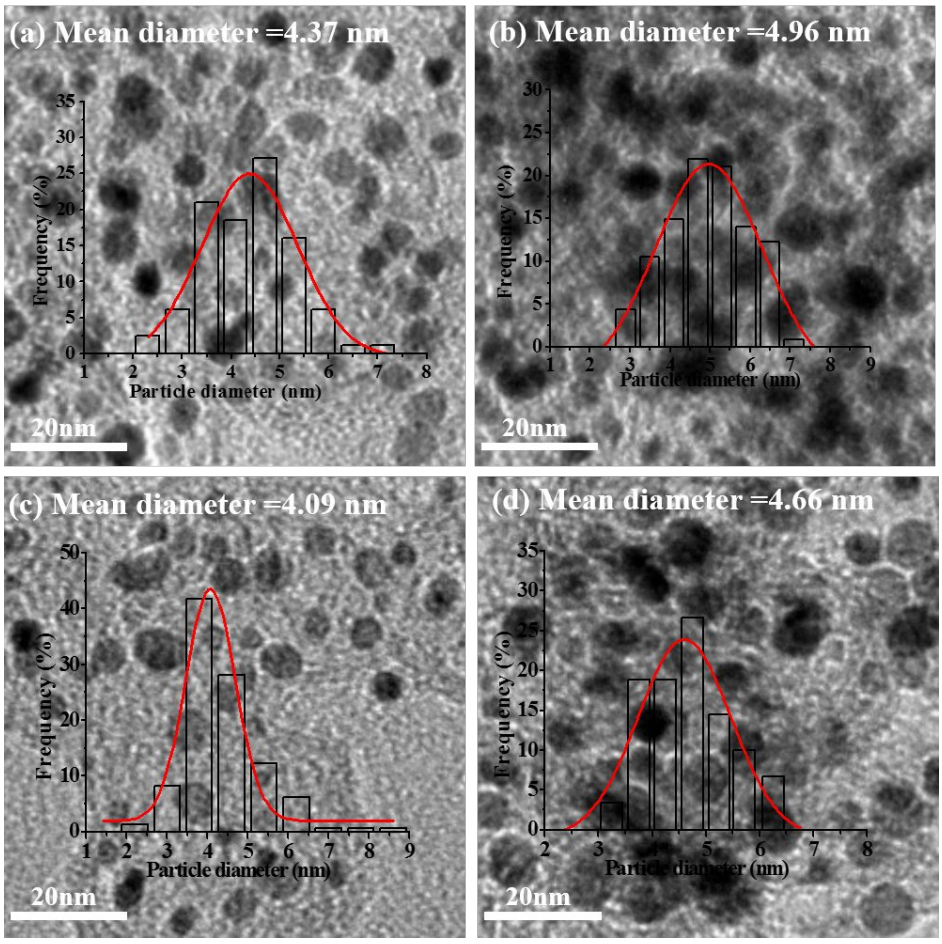


Figure S4. Representative TEM images and the corresponding histograms of particle diameter distribution (insets) for Pt/C electrocatalyst in MEAs at the 0 (a), 30,000 (b) ADT cycles and PtCo/C electrocatalyst in MEAs at the 0 (c), 30,000 (d) ADT cycles.

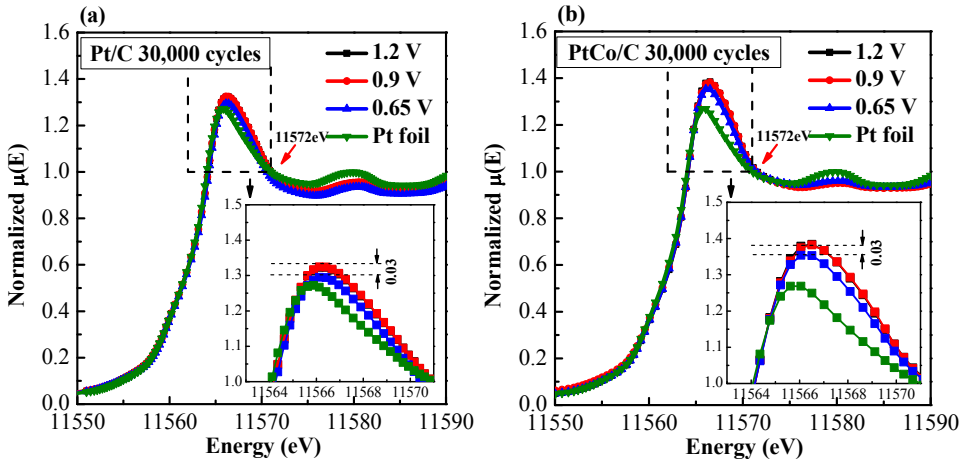


Figure S5. XANES spectra at the Pt L_3-edge for Pt/C (a) and PtCo/C (b) electrocatalysts at the 30,000 ADT cycles with different potential. The data for Pt foil (green line) are shown in each figure. The inset in each figure is an expanded view of the main peak region indicated by the rectangle.

Table S1. Structure parameters for Pt/C electrocatalyst as obtained from in situ Pt L_3-edge XAFS experiments with different potential at the 0, and 30,000 ADT cycles. Amp fixed at 0.84 for Pt, as obtained by fitting the Pt foil. Fits were done in R-space, $K^{1,2,3}$ weighting. For Pt, 1.5 < R < 3.2 Å and Δ K= 3.6 – 13.5 $Å^{-1}$ was used.

Pt/C		Pt-Pt			Pt-O			R-factor
ADT cycles	Potentials	CN	R (Å)	σ^2(10^{-3} $Å^{-1}$)	CN	R (Å)	σ^2(10^{-3} $Å^{-1}$)	
0 cycles	1.2 V	9.7 ± 0.4	2.765 ± 0.002	5.13	1.1 ± 0.3	1.973 ± 0.023	6.30	0.008
	0.9 V	9.7 ± 0.4	2.765 ± 0.002	5.12	0.9 ± 0.4	1.977 ± 0.032	6.30	0.010
	0.65 V	10.5 ± 0.4	2.764 ± 0.002	5.08	0.9 ± 0.4	1.975 ± 0.036	6.30	0.009
30,000 cycles	1.2 V	8.4 ± 0.4	2.764 ± 0.002	5.25	1.7 ± 0.3	1.925 ± 0.016	10.77	0.004
	0.9 V	8.8 ± 0.4	2.766 ± 0.001	5.20	1.6 ± 0.3	1.917 ± 0.015	10.60	0.002
	0.65 V	8.9 ± 0.4	2.766 ± 0.005	5.30	1.4 ± 0.8	1.919 ± 0.039	10.10	0.004

Table S2. Structure parameters for PtCo/C electrocatalyst as obtained from in situ Pt L_3-edge XAFS experiments with different potential at the 0, and 30,000 ADT cycles. Amp fixed at 0.84 for Pt, as obtained by fitting the Pt foil. Fits were done in R-space, $K^{1,2,3}$ weighting. For Pt, 1.4 < R < 3.1 Å and Δ K= 2.8 – 12.5 $Å^{-1}$ was used.

PtCo/C		Pt-Pt			Pt-Co			Pt-O			R-factor
ADT cycles	Potentials	CN	R (Å)	σ^2 (10^{-3} $Å^{-1}$)	CN	R (Å)	σ^2 (10^{-3} $Å^{-1}$)	CN	R (Å)	σ^2 (10^{-3} $Å^{-1}$)	
0 cycles	1.2 V	6.3 ± 0.2	2.712 ± 0.002	6.39	1.6 ± 0.1	2.683 ± 0.004	6.88	1.0 ± 0.1	2.001 ± 0.004	3.47	0.001
	0.9 V	6.5 ± 0.2	2.709 ± 0.002	6.07	1.7 ± 0.1	2.688 ± 0.003	5.97	0.8 ± 0.1	2.001 ± 0.006	3.47	0.002

	0.65 V	6.8 ± 0.6	2.716 ± 0.006	6.39	1.5 ± 0.3	2.687 ± 0.016	6.88	0.8 ± 0.2	2.007 ± 0.017	3.47	0.009
	1.2 V	6.5 ± 0.2	2.724 ± 0.002	5.88	1.3 ± 0.1	2.681 ± 0.006	6.00	0.9 ± 0.1	2.007 ± 0.006	3.92	0.001
30,000											
cycles	0.9 V	6.5 ± 0.2	2.722 ± 0.002	6.20	1.3 ± 0.1	2.687 ± 0.004	6.00	0.8 ± 0.1	2.006 ± 0.005	3.67	0.003
	0.65 V	6.8 ± 0.4	2.725 ± 0.002	5.75	1.3 ± 0.1	2.681 ± 0.005	6.00	0.7 ± 0.1	2.010 ± 0.007	3.92	0.001

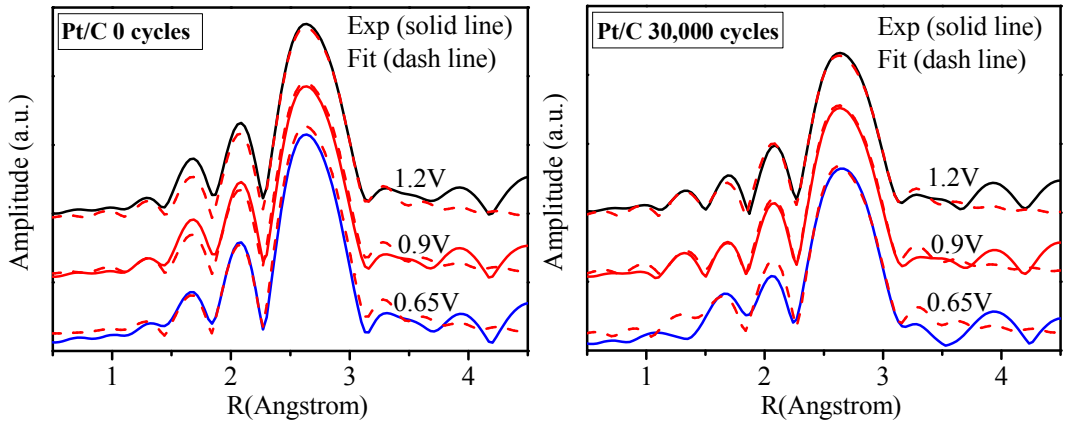


Figure S6. The R-space experiment (solid line) and fitting data (dash line) of Pt L_3-edge XAFS for Pt/C electrocatalyst with the different potential at the 0, and 30,000 ADT cycles.

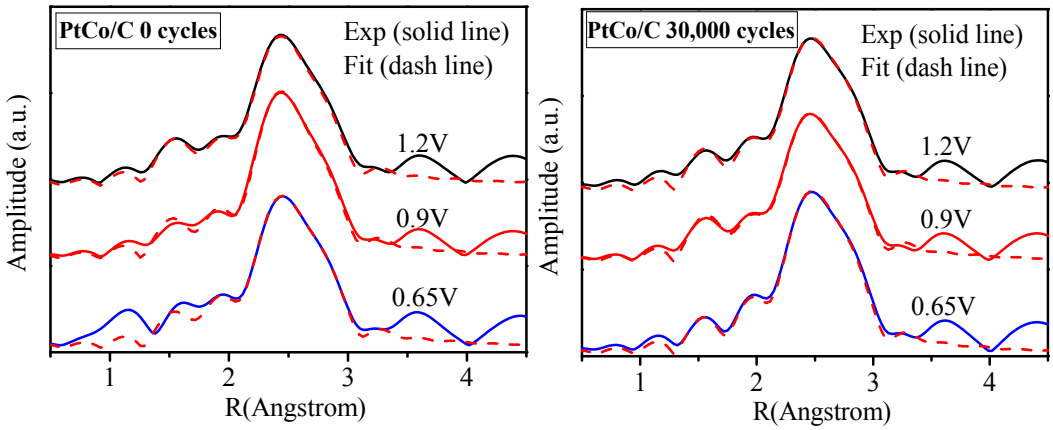


Figure S7. The R-space experiment (solid line) and fitting data (dash line) of Pt L_3-edge XAFS for PtCo/C electrocatalyst with the different potential at the 0, and 30,000 ADT cycles.

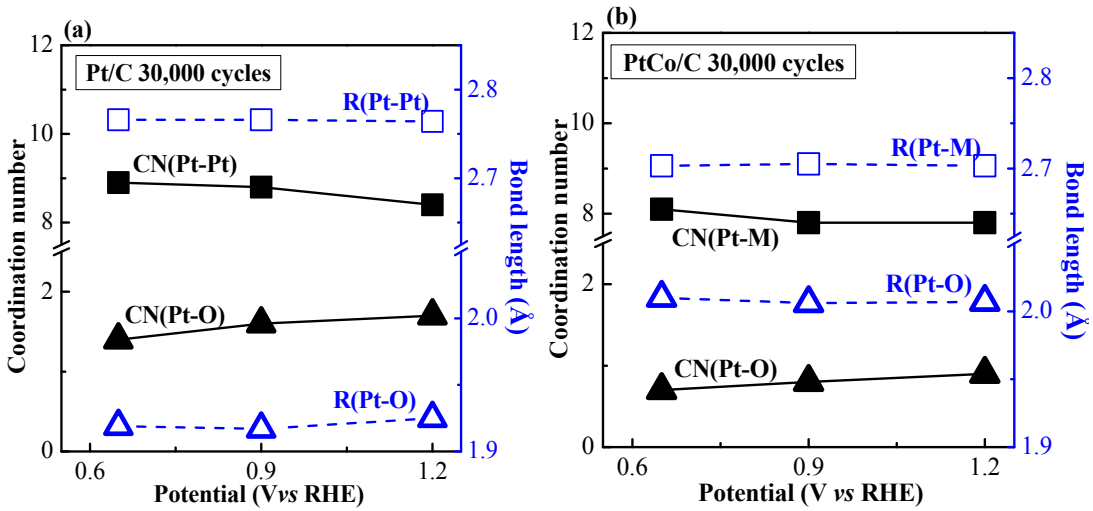


Figure S8. The coordination number and bond length of the first shell of Pt absorber at the Pt L_3-edge EXAFS spectra as a function of potential for Pt/C (a) and PtCo/C (b) electrocatalysts at the 30,000 ADT cycles.

Table S3. Structure parameters for PtCo/C electrocatalyst as obtained from in situ Co K-edge XAFS experiments with different potential at the 0, and 30,000 ADT cycles. Amp fixed at 0.79 for Co, as obtained by fitting the Co foil. Fits were done in R-space, $K^{1,2,3}$ weighting. For Co, 1.5 < R < 3.1 Å and Δ K= 3.5 – 12.8 $Å^{-1}$ was used.

PtCo/C		Co-Co			Co-Pt			Co-O			
ADT cycles	Potentials	CN	R (Å)	σ^2 (10^{-3} $Å^{-1}$)	CN	R (Å)	σ^2 (10^{-3} $Å^{-1}$)	CN	R (Å)	σ^2 (10^{-3} $Å^{-1}$)	R-factor
0 cycles	0.9 V	1.0± 0.1	2.666 ± 0.006	1.90	6.1 ± 0.4	2.688 ± 0.003	5.97	0.9 ± 0.1	2.0141± 0.014	6.22	0.002
30,000 cycles	0.9 V	0.8± 0.1	2.664 ± 0.008	0.98	5.6 ± 0.5	2.687± 0.004	6.00	1.5 ± 0.1	2.134 ± 0.010	3.94	0.003

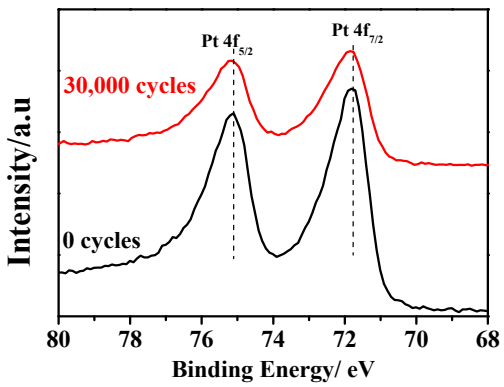


Figure S9 XPS spectra in the Pt 4f regions for Pt/C electrocatalysts at the 0 (black line), and 30,000 (red line) ADT cycles.

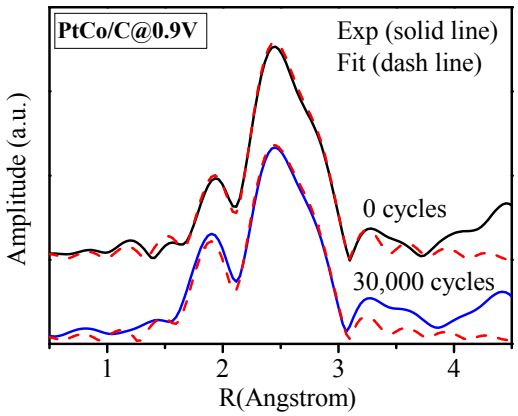


Figure S10. The R-space experiment (solid line) and fitting data (dash line) of Co K-edge XAFS for PtCo/C electrocatalyst at 0.9 V at the 0, and 30,000 ADT cycles.

Table S4. ICP-AES for PtCo/C electrocatalysts in MEAs.

Molar ratio	0 cycles	30,000 cycles
X_{Co}/X_{Pt}	0.19	0.16