Electronic Supporting Information

Highly Active Hydrogen Evolution Catalysis on Oxygen-Deficient Double-Perovskite Oxide $PrBaCo_2O_{6-\delta}$

H. Togano,[1] K. Asai,[1] S. Oda,[1]
H. Ikeno,[1] S. Kawaguchi,[2] K. Oka,[3] K. Wada,[4] S. Yagi,[5] I. Yamada,[1]*

[1]Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-2 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8570, Japan

[2]Japan Synchrotron Radiation Research Institute (JASRI), 1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

[3]Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1 Kowakae, Higashi-Osaka, Osaka, 577-8502, Japan

[4]Fuji Die Co., Ltd., 36-1 Hirasawa, Hadano, Kanagawa 257-0015, Japan

[5]Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

Table S1. Oxygen deficiency content determined by iodometry (δ) and specific surface areas determined by BET analysis of Kr gas adsorption data (A_s) for $PBCO_{6-\delta}$.

Compound	δ	A_s ($m^2\ g^{-1}$)
$PBCO_{5.15}$	0.85(3)	1.01
$PBCO_{5.5}$	0.49(5)	1.17
$PBCO_{5.7}$	0.31(8)	1.71
$PBCO_{5.8}$	0.21(3)	0.47
$PBCO_{5.9}$	0.09(1)	1.54
$PBCO_6$	–0.01(7)	1.27

Table S2. Structure parameters obtained from Rietveld refinement of synchrotron XRD for PBCO$_{6-\delta}$ (δ = 0, 0.1, 0.2, 0.3, and 0.85).

	PBCO$_6$	PBCO$_{5.9}$	PBCO$_{5.8}$	PBCO$_{5.7}$	PBCO$_{5.15}$
Space group	*P*4/*mmm*	*P*4/*mmm*	*P*4/*mmm*	*P*4/*mmm*	*P*4/*mmm*
a (Å)	3.87998(9)	3.88653(14)	3.90985(3)	3.90541(10)	3.95064(7)
c (Å)	7.6684(2)	7.6641(3)	7.63046(5)	7.63559(2)	7.60207(13)
z (Co)	0.2487(4)	0.2493(7)	0.24977(16)	0.2486(4)	0.2472(3)
z (O3)	0.2323(7)	0.2287(10)	0.2207(3)	0.2219(5)	0.2034(5)
g (O1)	1	0.86(2)	0.775(7)	0.796(14)	0.175(13)
U_{iso}(Pr)×1000 (Å^2)	2.98(10)[a]	4.9(9)	8.6(2)	4.28(11)[a]	5.1(3)
U_{iso}(Ba)×1000 (Å^2)	2.98(10)[a]	1.3(9)	4.2(2)	4.28(11)[a]	7.1(4)
U_{iso}(Co)×1000 (Å^2)	1.96(14)	1.7(2)	3.53(9)	1.70(15)	4.9(2)
U_{iso}(O1)×1000 (Å^2)	9.6(5)[a]	1.02(10)[b]	11.2(4)[c]	8.4(7)[a]	13.3(9)[b]
U_{iso}(O2)×1000 (Å^2)	9.6(5)[a]	10.2(10)[b]	11.2(4)[c]	8.4(7)[a]	13.3(9)[b]
U_{iso}(O3)×1000 (Å^2)	9.6(5)[a]	10.2(10)[b]	11.2(4)[c]	8.4(7)[a]	13.3(9)[b]
R_{wp} (%)	7.362	11.057	5276	6.285	10.992
R_{B} (%)	1.671	1.900	0.997	1.948	1.807
S	1.1920	1.6239	1.3234	0.7253	1.2549

Atomic sites: Pr 1*a* (0, 0, 0), Ba 1*b* (0, 0, $^1/_2$), Co 2*h* ($^1/_2$, $^1/_2$, *z*), O1 1*c* ($^1/_2$, $^1/_2$, 0), O2 1*d* ($^1/_2$, $^1/_2$, $^1/_2$), O3 4*i* (0, $^1/_2$, *z*); The occupancy factors *g* for Pr, Ba, Co, O2, and O3 sites were fixed at unity.

[a] The following constraints were adopted for PBCO$_6$ and PBCO$_{5.7}$: U_{iso}(Pr) = U_{iso}(Ba); U_{iso}(O1) = U_{iso}(O2) = U_{iso}(O3).

[b] The following constraints were adopted for PBCO$_{5.9}$, PBCO$_{5.8}$: U_{iso}(O1) = U_{iso}(O2) = U_{iso}(O3).

Table S3. Structure parameters obtained from Rietveld refinement of synchrotron XRD for $\mathrm{PBCO}_{5.5}$.

	site	*g*	*x*	*y*	*z*	$U_{\mathrm{iso}}\times1000$ (Å^2)
Pr1	2*t*	1[a]	½	½	0.26762(16)	3.1(3)
Ba1	2*s*	1[a]	½	0	0.5145(15)	4.7(4)
Co1	2*n*	1[a]	0	0.2504(5)	½	3.2(3)[b]
Co2	2*m*	1[a]	0	0.2516(5)	0	3.2(3)[b]
O1	1*a*	1[a]	0	0	0	10.5(10)[b]
O2	1*c*	1[a]	0	0	½	10.5(10)[b]
O3	1*g*	0.90(2)	0	½	½	10.5(10)[b]
O4	1*e*	0.06(2)	0	½	0	10.5(10)[b]
O5	2*o*	1[a]	½	0.3090(17)	0	10.5(10)[b]
O6	2*p*	1[a]	½	0.2751(19)	½	10.5(10)[b]
O7	4*u*	1[a]	0	0.2407(10)	0.2841(12)	10.5(10)[b]

Space group: *Pmmm* (No. 47); $a = 3.90927(8)$ Å, $b = 7.88417(18)$ Å, $c = 7.60315(16)$ Å; $R_{\mathrm{wp}} = 10.648\%$, $R_{\mathrm{B}} = 1.786\%$, $S = 1.2905$.

[a] The occupancy factors for Pr1, Ba1, Co1, Co2, O1, O2, O5, O6, and O7 sites were fixed to the unity.

[b] The following constraints were adopted: $U_{\mathrm{iso}}(\mathrm{Co1}) = U_{\mathrm{iso}}(\mathrm{Co2})$; $U_{\mathrm{iso}}(\mathrm{O1}) = U_{\mathrm{iso}}(\mathrm{O2}) = U_{\mathrm{iso}}(\mathrm{O3}) = U_{\mathrm{iso}}(\mathrm{O4}) = U_{\mathrm{iso}}(\mathrm{O5}) = U_{\mathrm{iso}}(\mathrm{O6}) = U_{\mathrm{iso}}(\mathrm{O7})$.

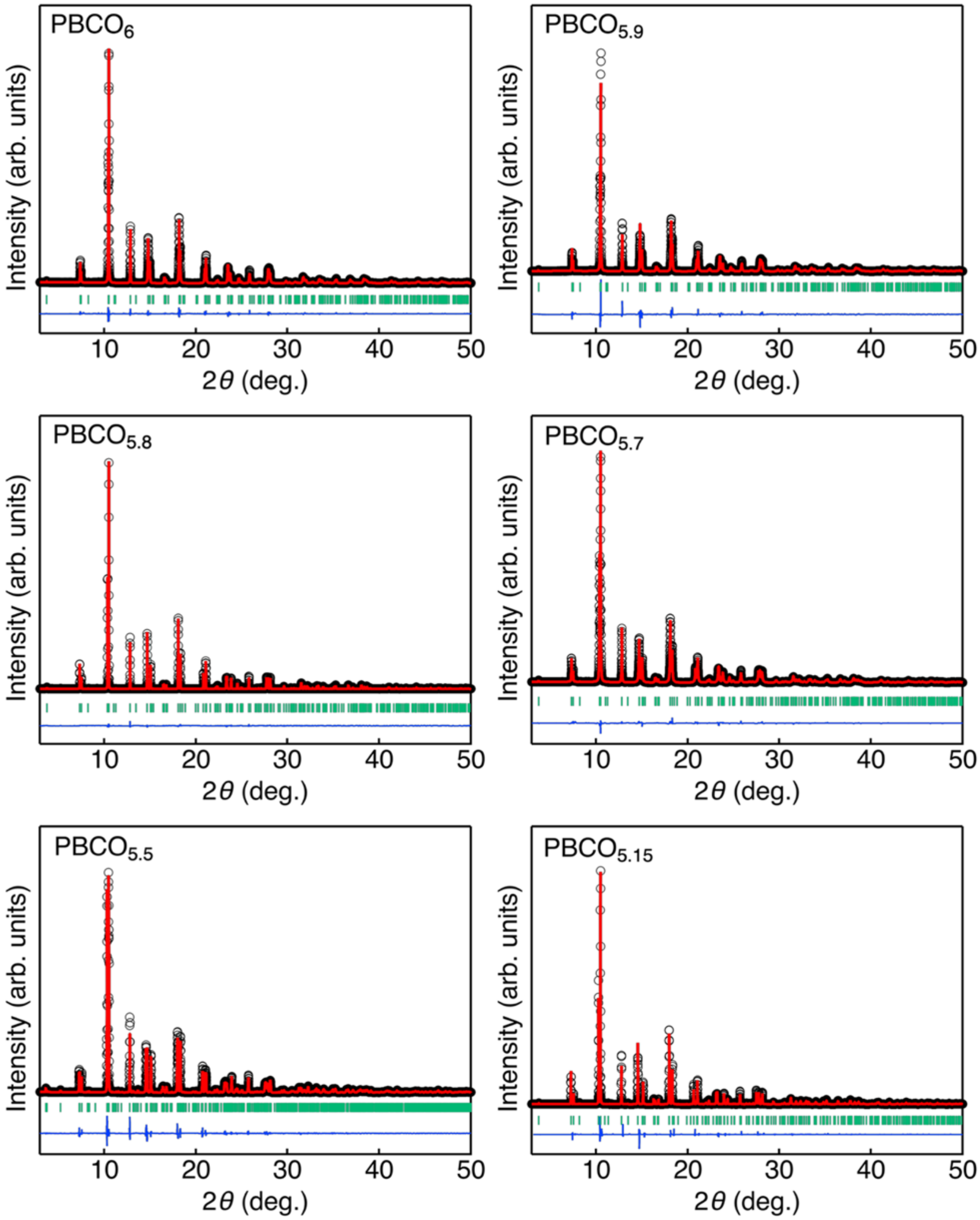

Figure S1. Rietveld refinement results of the SXRD for PBCO$_{6-\delta}$ (δ = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.85). Circles (black) and solid lines (red) represent observed and calculated patterns, respectively. The difference between the observed and calculated patterns is shown at the bottom (blue). The vertical marks (green) indicate the Bragg reflection positions of PBCO$_{6-\delta}$.

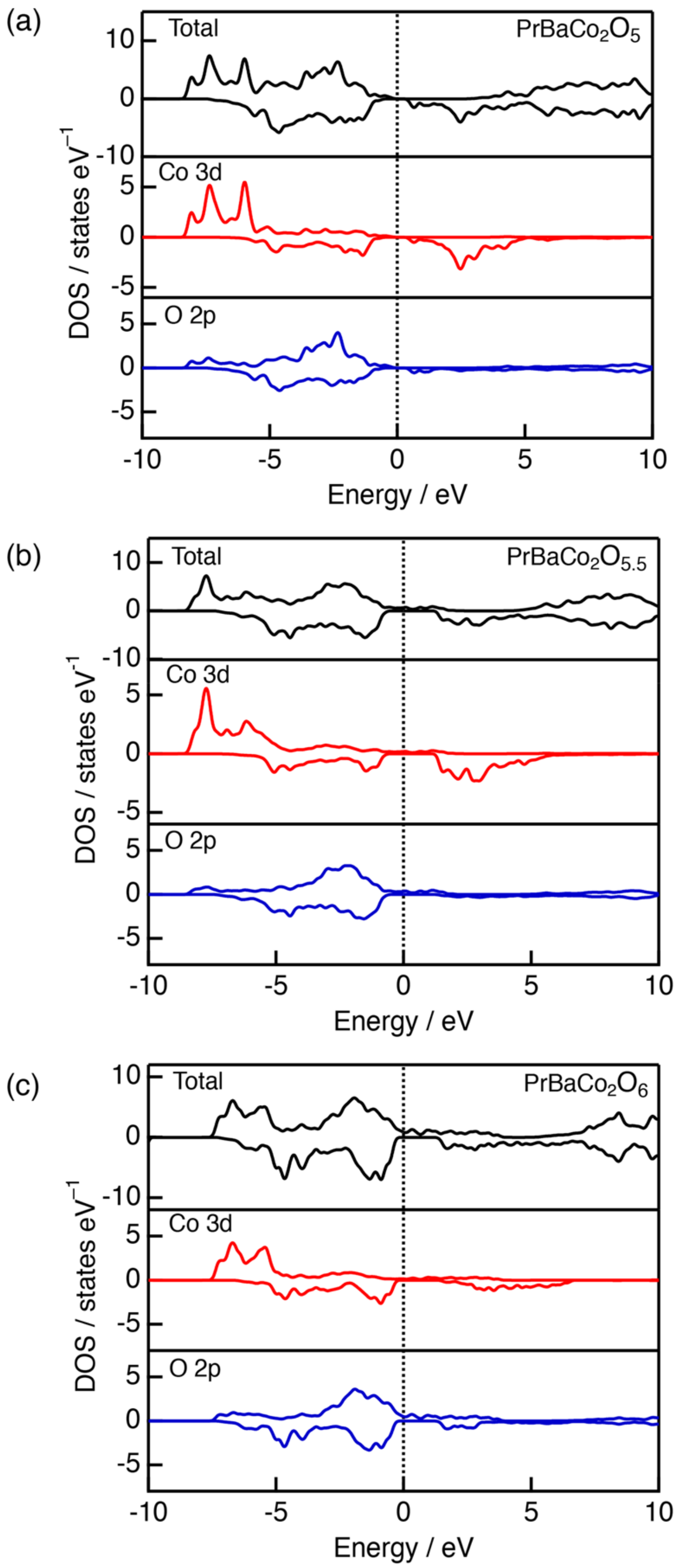

Figure S2. Total and partial density of states (DOS) in wide range for PBCO$_{6-\delta}$ obtained from DFT calculation: (a) $\delta = 1$, (b) $\delta = 0.5$, and (c) $\delta = 0$.

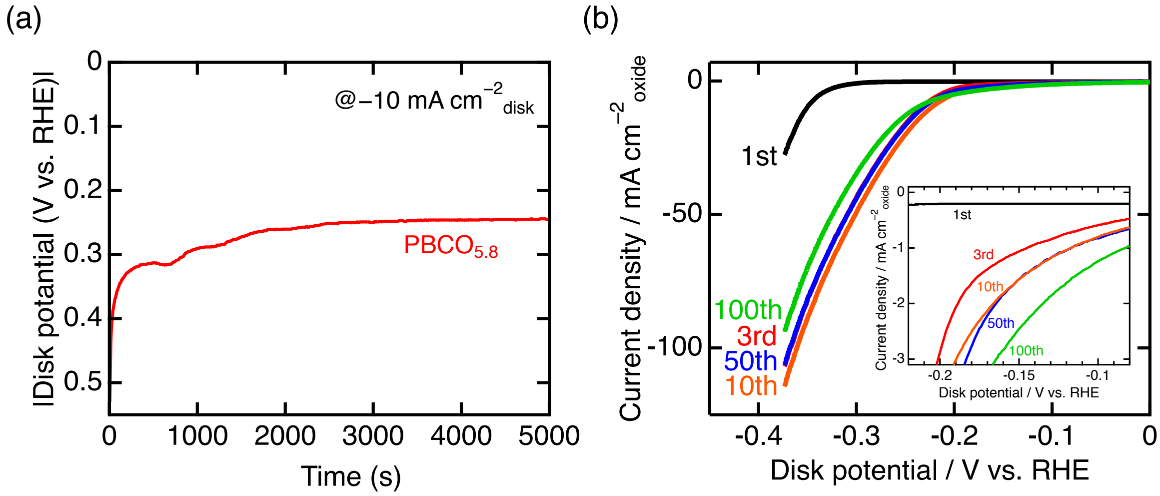

Figure S3. (a) Chronopotentiogram for PBCO$_{5.8}$ measured in 1 M KOH aqueous solution at -10 mA cm$^{-2}_{\mathrm{disk}}$. (b) Continuous cyclic voltammograms (cathodic scans only) for PBCO$_{5.8}$ at 1st, 3rd, 10th, 50th, and 100th cycle.

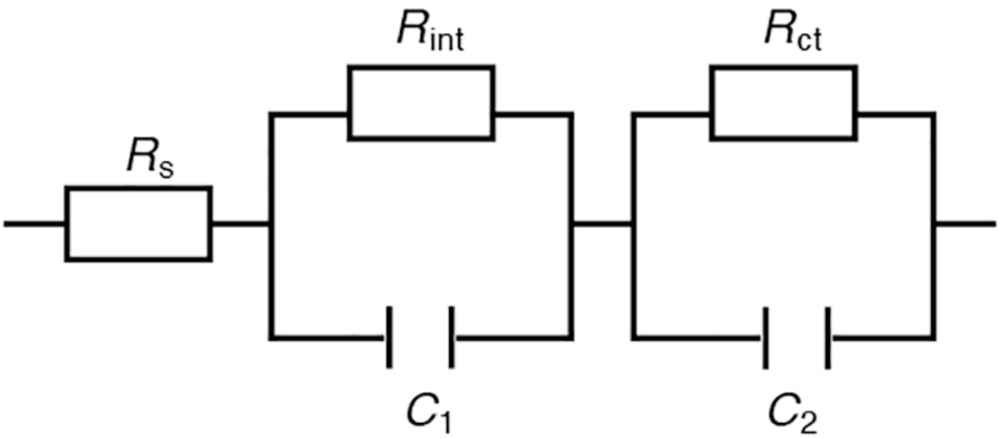

Figure S4. Equivalent circuit for fitting the EIS data. R_s: electrolyte resistance, R_{int}: interface resistance, R_{ct}: charge-transfer resistance, C_1: capacitance arisen from the interface, and C_2: capacitance generated from the Faradic process.