Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# B-site doping effects of $NdBa_{0.75}Ca_{0.25}Co_2O_{5+\delta}$ double perovskite catalysts for oxygen evolution and reduction reactions

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## Supplementary Figures

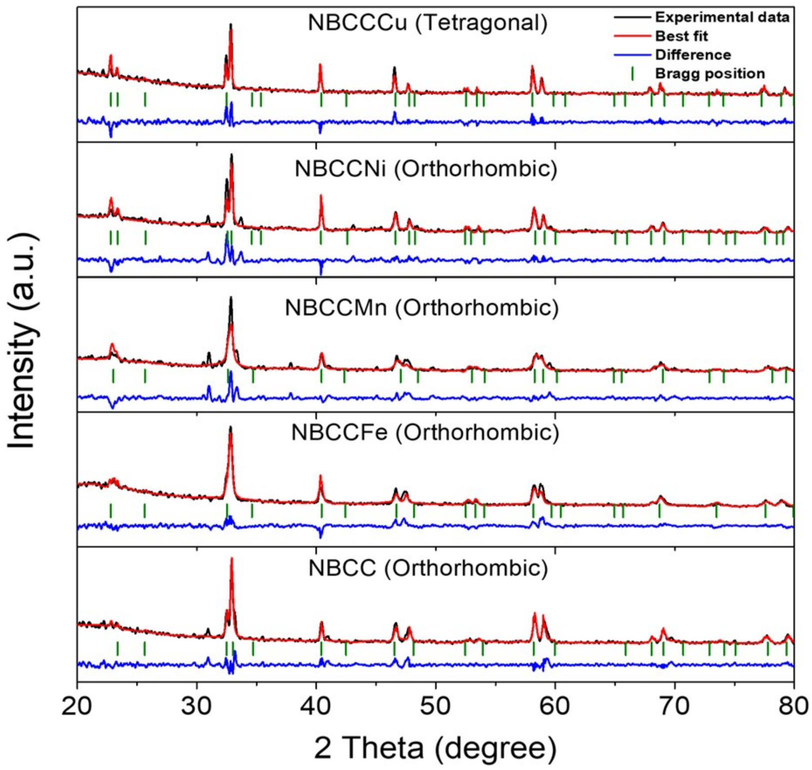


Fig. S1. Rietveld refinements of NBCC-based catalysts processed by the Fullprof program.

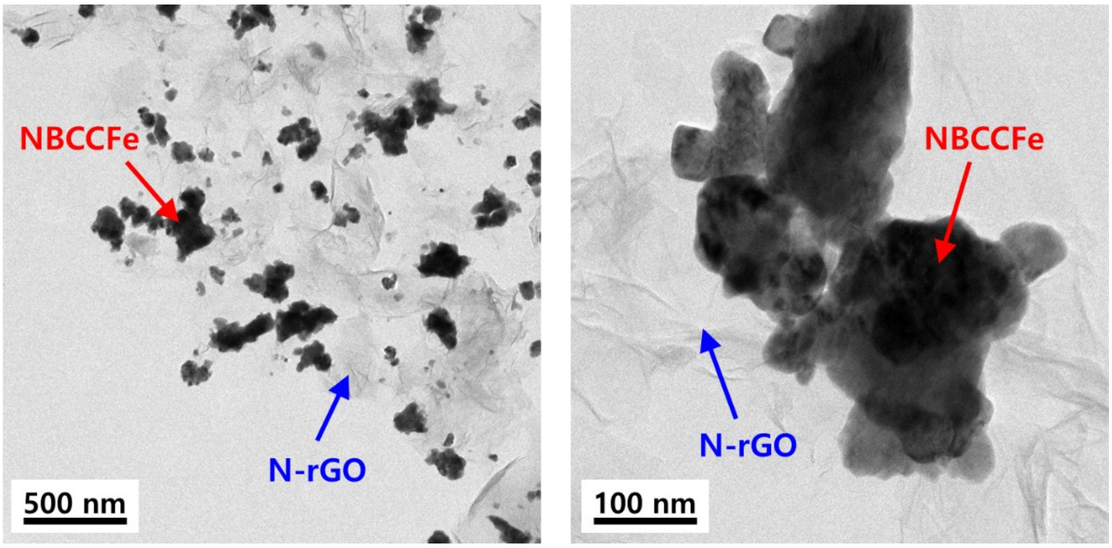


Fig. S2. Morphological characteristics of NBCCFe/N-rGO hybrid catalyst analyzed by HRTEM.

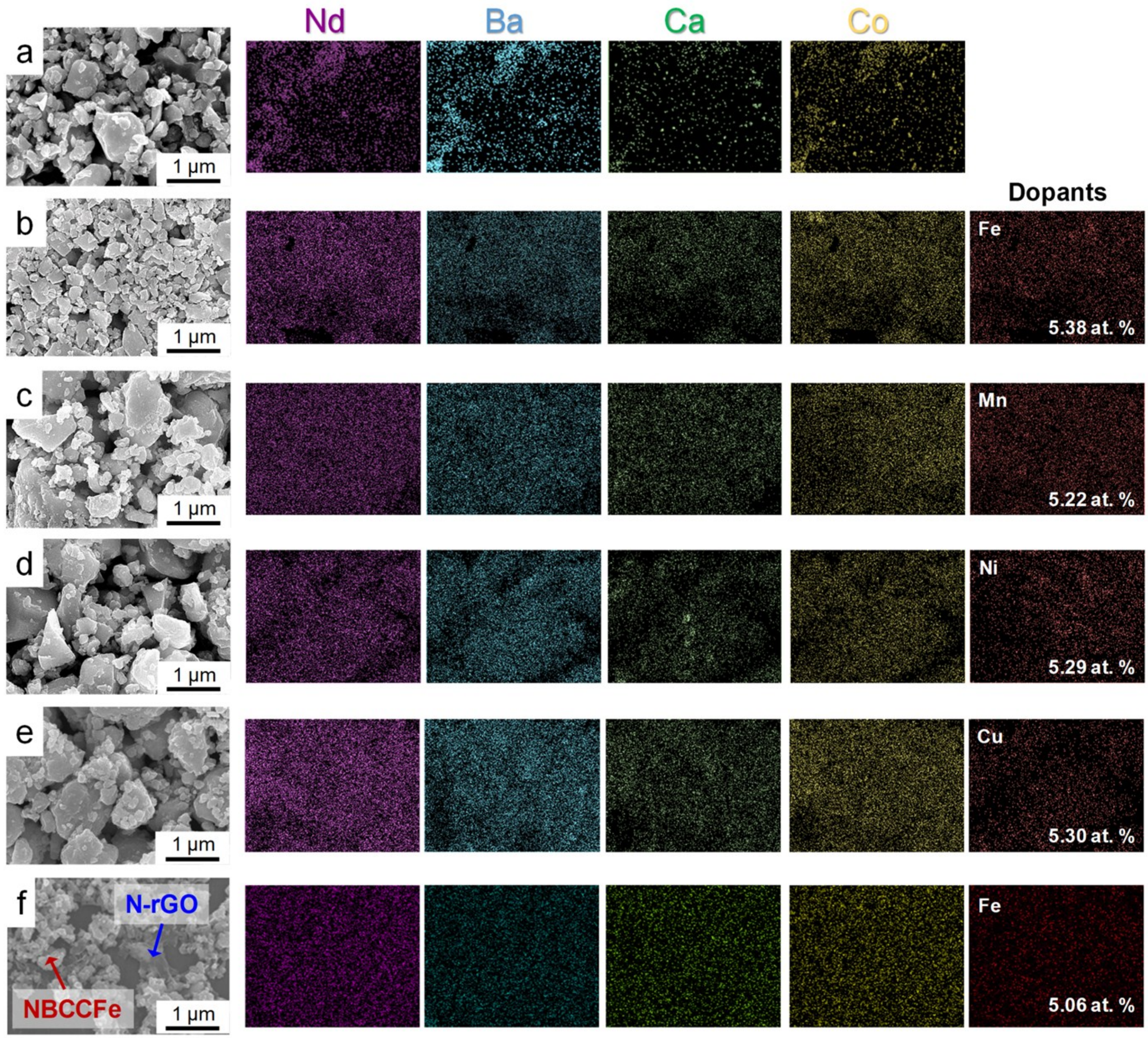


Fig. S3. Surface morphology and distribution of elemental compositions of catalysts by FE-SEM and EDX mapping: (a) NBCC (b) NBCCFe (c) NBCCMn (d) NBCCNi, (e) NBCCCu, and (f) NBCCFe/N-rGO.

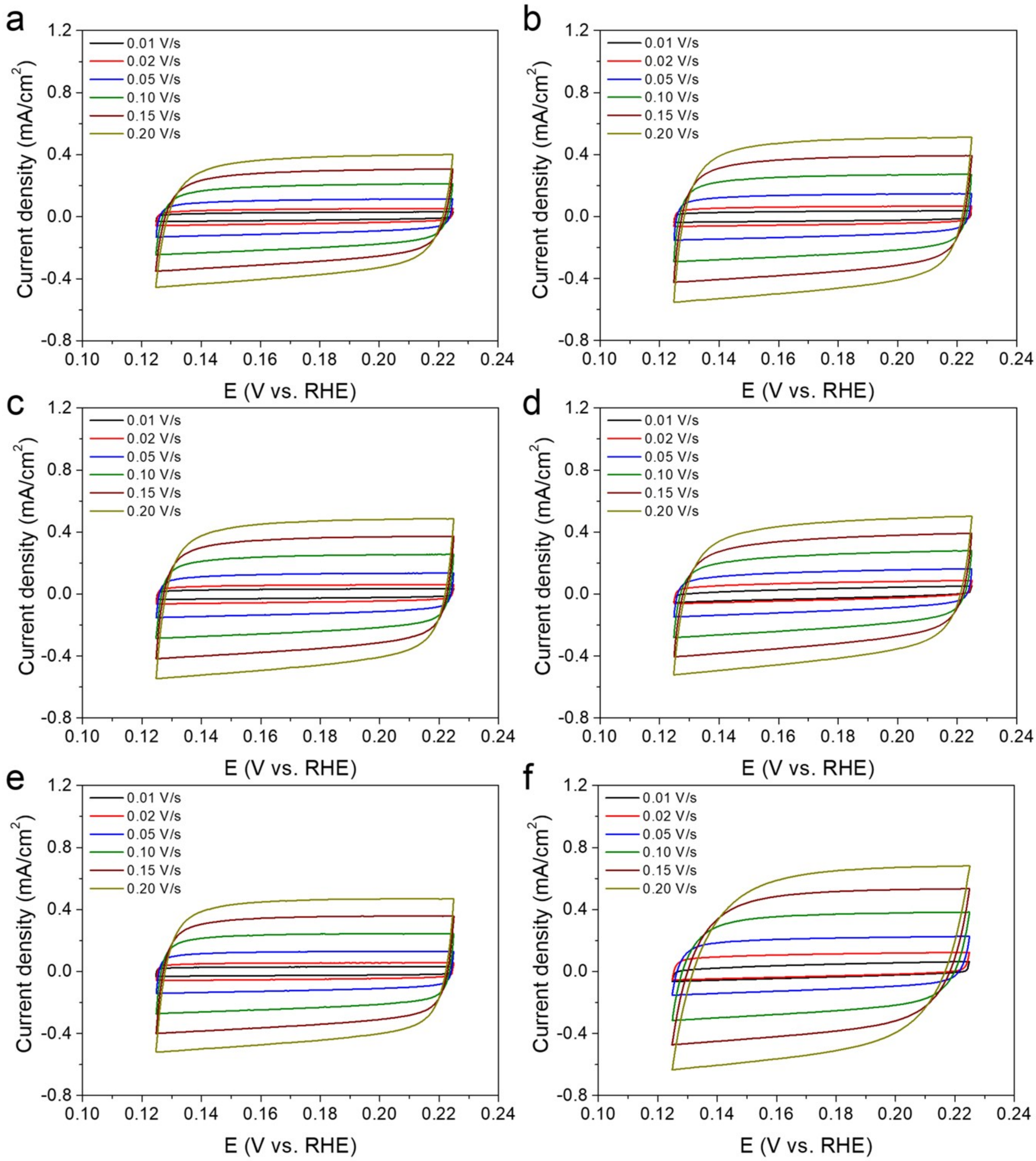


Fig. S4. Cyclic voltammogram curves of the catalysts with different scan rates (10-200 mV·s$^{-1}$). (a) NBCC, (b) NBCCFe, (C) NBCCMn, (d) NBCCNi, (e) NBCCCu, and (f) NBCCFe/N-rGO.

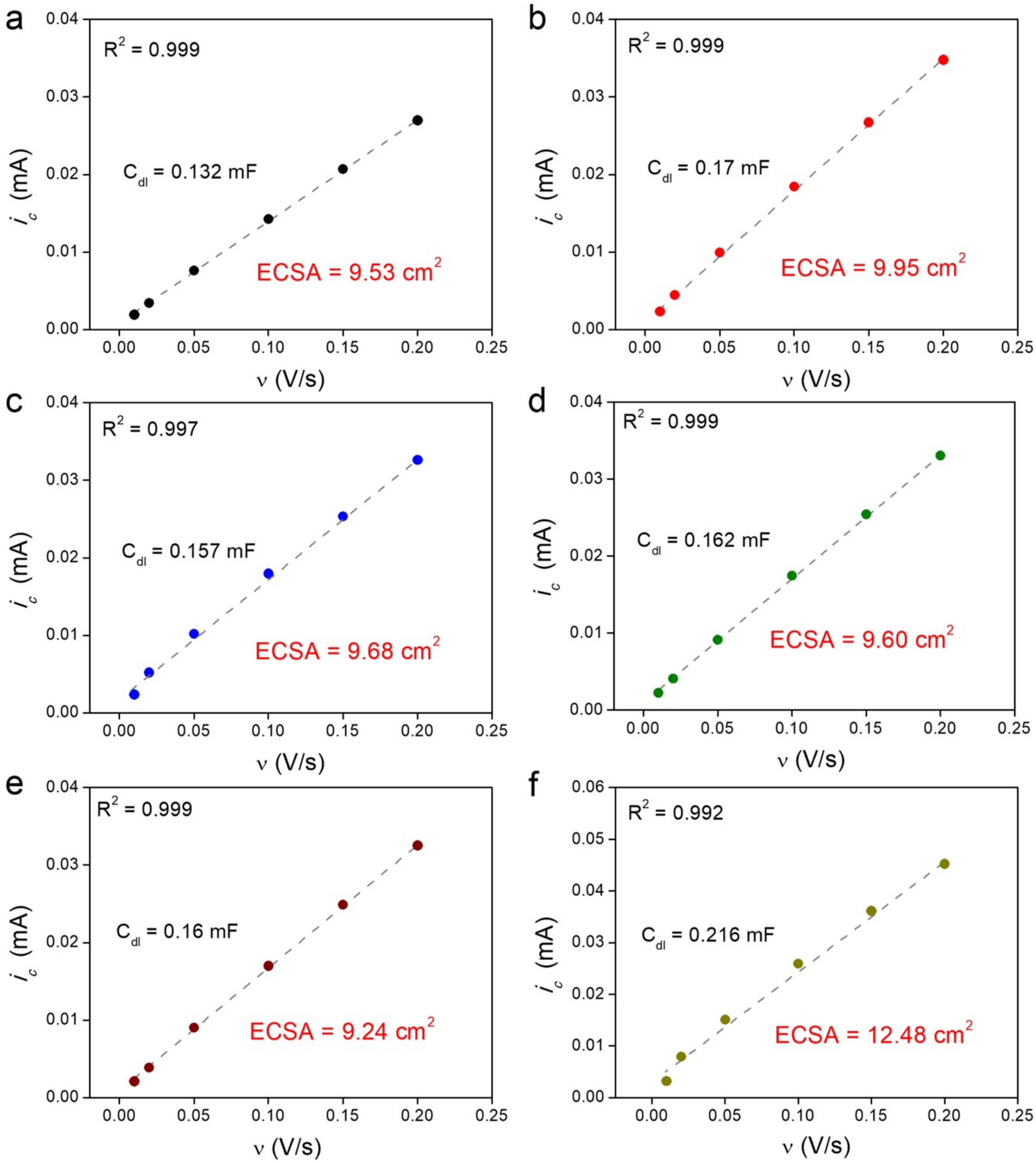


Fig. S5. Linear plots for the measured charging current ($i_c$) versus scan rate for calculation of the ECSA. (a) NBCC, (b) NBCCFe, (C) NBCCMn, (d) NBCCNi, (e) NBCCCu, and (f) NBCCFe/N-rGO. Double layer capacitances of the materials were determined from the linear plots.

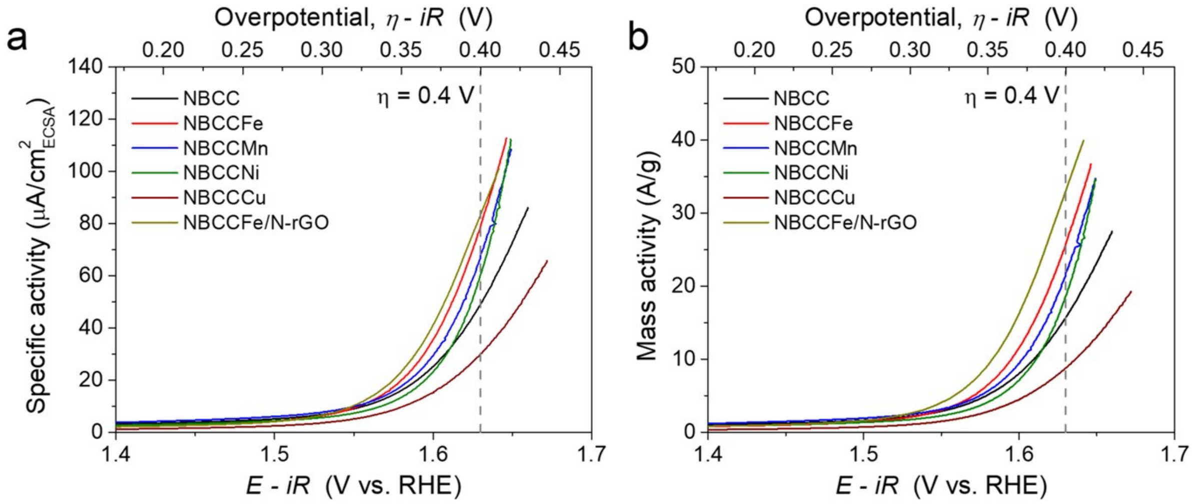


Fig. S6. (a) Specific activity ($\mu A \cdot cm^{-2}{}_{ECSA}$) and (b) mass activity ($A \cdot g^{-1}$) of catalysts in OER polarization curves normalized by the ECSA at $\eta$ = 0.4 V in 0.1 M KOH solution.

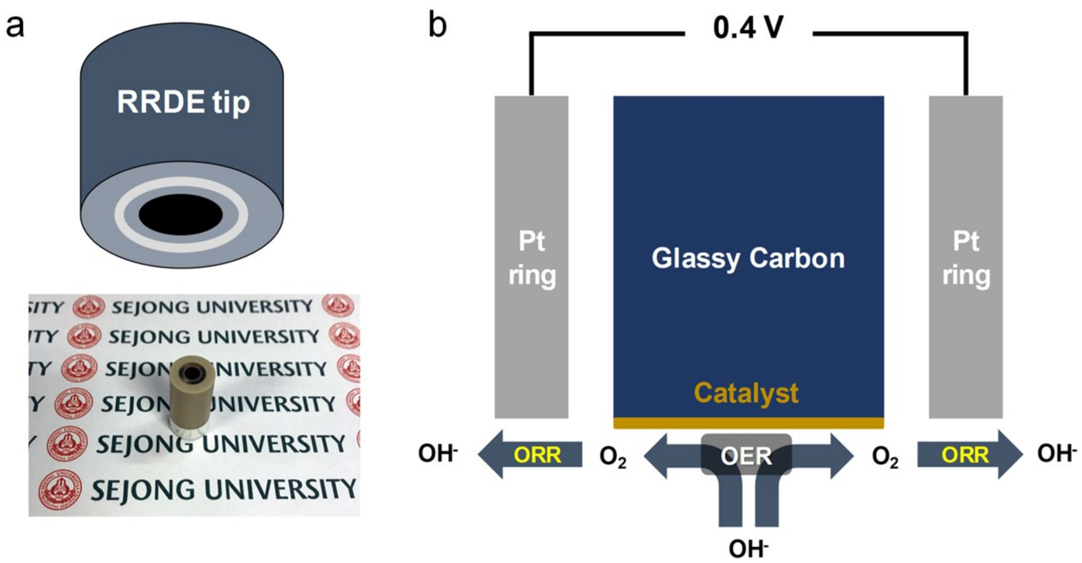


Fig. S7. (a) Schematic illustration (top) and Actual photograph (bottom) of the RRDE tip. (b) The continuous OER (disk) to ORR (ring) process initiated on a RRDE ($N_2$-saturated 0.1 M KOH, ring potential: 0.40 V).

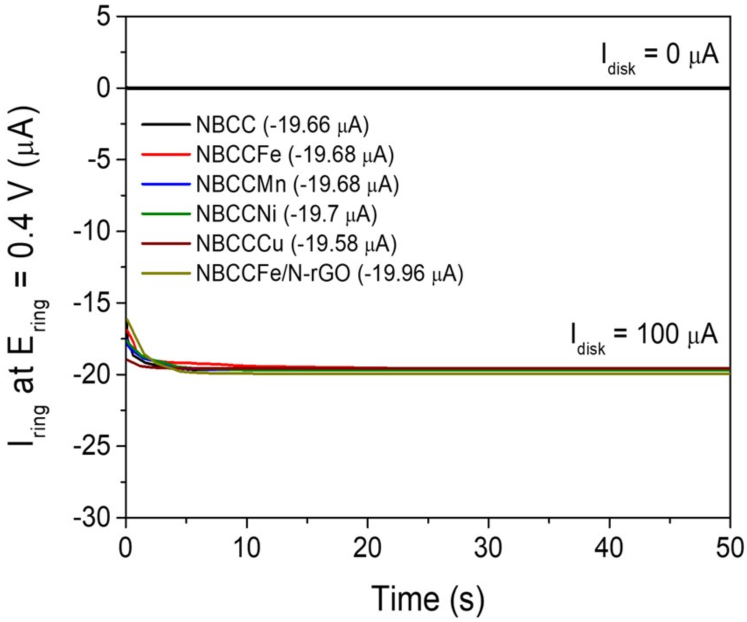


Fig. S8. The ring currents of NBCC-based catalysts on a RRDE (1,600 rpm) in 0.1 M KOH solution (ring potential: 0.40 V).

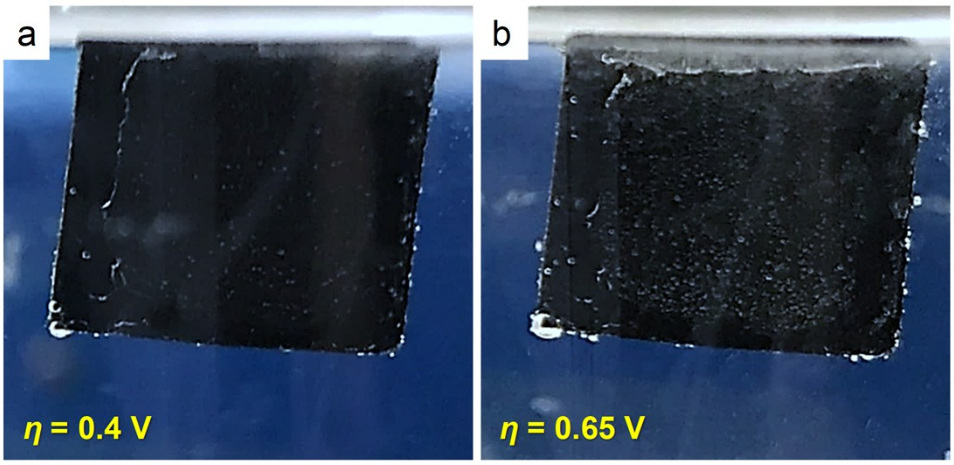


Fig. S9. Images of oxygen bubble generation in a large-scale water electrolysis half-cell (1 $cm^2$) using the NBCCFe catalyst at η = 0.4 V (left) and η = 0.65 V (right).

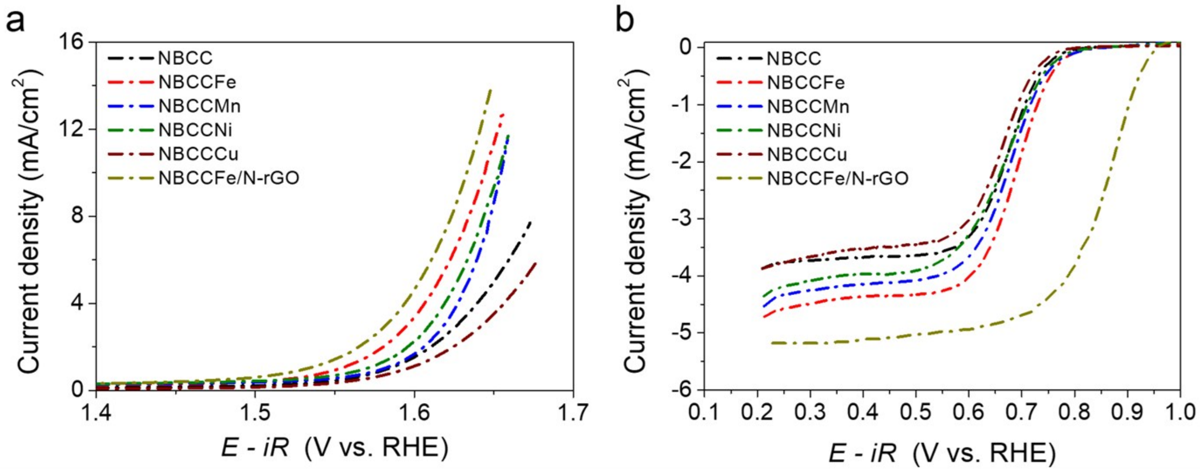


Fig. S10. 1,500th OER polarization curves and 10,000th ORR polarization curves of NBCC and doped-NBCC catalysts.

## 2. Supplementary Tables

Table S1. Comparison of oxygen activity of NBCCFe and NBCCFe/N-rGO with reported perovskite-based electrocatalysts.

| Catalysts | $E_{ORR}$ (V) at $j$ = -3 mA cm$^{-2}$ | $E_{OER}$ (V) at $j$ = 10 mA cm$^{-2}$ | Oxygen activity [a] (V) | Reference |
|---|---|---|---|---|
| NBCCFe/N-rGO | 0.848 | 1.609 | 0.761 | This Work |
| NBCCFe | 0.679 | 1.627 | 0.948 | This Work |
| Core-Corona $LaNiO_3$/N-CNT | 0.64 | 1.67 | 1.03 | Nano Lett. 2012, 12, 1946 (Ref. 1) |
| $La_{0.3}(Ba_{0.5}Sr_{0.5})_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$/KB | 0.58 | 1.59 | 1.01 | Angew. Chem. Int. Ed. 2014, 53, 4582 (Ref. 2). |
| porous $CaMnO_3$ | 0.8 | 1.81 | 1.01 | Adv. Mater. 2014, 26, 2047 (Ref. 3). |
| Ar treated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$/KB | 0.62 | 1.77 | 1.05 | Adv. Energy Mater. 2015, 5, 1501560 (Ref. 4) |
| $LaTi_{0.65}Fe_{0.35}O_{3-\delta}$/N-CNR | 0.72 | 1.77 | 1.05 | Nano Energy 2015, 15, 92 (Ref. 5). |
| $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$-PR/N-rGO | 0.81 | 1.73 | 0.92 | Nano Energy 2014, 10, 192 (Ref. 6). |
| $La_{0.58}Sr_{0.4}Fe_{0.2}Co_{0.8}O_3$/N-CNT | 0.7 | 1.63 | 0.93 | Electrochimica Acta 2016, 208, 25 (Ref. 7). |
| Multi-shelled $La_{0.9}Sr_{0.1}CoO_3$ | 0.64 | 1.76 | 1.12 | J. Mater. Chem. A, 2015, 3, 22448 (Ref. 8). |
| $NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$/CB | 0.651 | 1.624 | 0.973 | J. Mater. Chem. A, 2017, 5, 13019 (Ref. 9). |
| $PrBa_{0.25}Sr_{0.75}Co_2O_{5+\delta}$/AB | 0.68 | 1.65 | 0.97 | Journal of Power Sources 2016, 334, 86 ((Ref. 10). |
| Mn-oxide film | 0.73 | 1.77 | 1.04 | J. Am. Chem. Soc. 2010, 132, 13612 (Ref. 11). |
| $Co_3O_4$/N,S-doped carbon | 0.82 | 1.61 | 0.79 | Adv. Funct. Mater. 2014, 24, 7655 (Ref. 12). |

| | | | | |
|---|---|---|---|---|
| $MnO_x$ on stainless steel mesh | 0.82 | 1.62 | 0.8 | Energy Environ. Sci. 2014, 7, 2017 (Ref. 13). |
| $Mn_xO_y$/N-doped Carbon | 1.68 | 0.81 | 0.87 | Angew. Chem. Int. Ed. 2014, 53, 8508 (Ref. 14). |
| CNT@NCNT | 0.65 | 1.73 | 1.08 | Adv. Funct. Mater. 2014, 24, 5956 (Ref. 15) |
| N-doped graphene/CNT | 0.64 | 1.65 | 0.96 | Small 2014, 10, 2251 (Ref. 16). |
| N,S,Fe-doped Carbon | 0.87 | 1.78 | 0.91 | J. Am. Chem. Soc. 2014, 136, 14486 (Ref. 17). |
| N-doped Carbon | 0.77 | 1.61 | 0.84 | Nat. Commun. 2013, 4, 2390 (Ref. 18). |

**References**


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