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Bimetallic Nanoparticle Decorated Perovskite Oxide for State-of-the-art Trifunctional Electrocatalysis

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ABSTRACT

The development of stable ABO₃ type perovskite oxides with trifunctional electrocatalytic activity is an arduous task. Such a feat is achieved by exsolution of the B-site cations to bimetallic nanoparticles (NPs) decorated on perovskite surface. $Sr_{0.95}Nb_{0.1}Co_{0.9.x}Ni_xO_{3-\delta}$ (0.1 $\leq x \leq 0.4$) was prepared by calcination at 1000°C and treated under 10% H₂/N₂ to create <30 nm Co-Ni exsolved NPs. Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) activities are facilitated with x = 0.1 composition whereas hydrogen evolution reaction (HER) activities such that the overpotentials drop by 58, 48 and 91 mV from their preceding parent compositions to 380, 347 and 208 mV at 10 mA cm⁻², -3 mA cm⁻² and -10 mA cm⁻² for OER, ORR and HER, respectively at pH 14. In terms of pH universality, HER overpotential is redressed to 183 mV at pH 0. The improved catalytic activity as compared to several reported perovskite oxide and non-perovskite based systems owes to the simultaneous regulation of an optimal e_g orbital filling, cation vacancies at catalytically active B-sites, lower metal-oxygen bond hybridization, oxygen non-stoichiometry, surface oxygen vacancies, ionic and charge-transfer abilities.

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Introduction

The increasing global demands for eco-friendly and low cost renewable storage and conversion technologies have propelled the advent of state-of-the-art electrocatalysts for devices such as metal-air batteries, fuel cells, and water electrolyzers.¹⁻³ While the fundamental challenges in terms of performance, cost and operational stability are major concerns, the sluggish kinetics of oxygen electrocatalytic reactions that limit the efficiency and power density of the devices need prime attention.^{4,5} Furthermore for cost reduction and system simplification in industrial applications, the development of homologous catalysts with multifunctional activity in OER, ORR and HER is technologically vital.^{1,6,7} Such a desirable catalyst should also work at lower overpotentials surpassing the benchmark precious metal/metal oxides.

In this context, the ABO₃ type perovskite oxides besides having interesting physical attributes,^{8,9} have emerged as cost-effective electrocatalysts due to their key properties such as generation of redox couples due to flexibility of metal oxidation states upon doping, tunable structural defects, high ionic conductivity, and fast oxygen exchange kinetics.^{10,11} For example, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- $\delta}$} (BSCF) has been highlighted as a strong candidate for ORR/OER,¹² and recently as HER catalyst,¹³ while in the early 1990s, Goodenough *et al.* reported Sr_{1-x}NbO_{3- δ} as HER catalyst in strong acids.¹⁴ Although perovskite oxides with structural and chemical flexibilities can catalyze OER/ORR efficiently, they were not studied extensively for HER catalysis. In the SrMO₃ (M = 3*d* transition metal) family, although SrNiO₃ is theoretically more covalent and catalytically active than SrCoO₃,¹⁵ the highly covalent Co 3*d* - O 2*p* bonding in SrCoO_{2.7} results in an improved OER activity.¹⁶ Nb doping in SrCoO₃ is particularly beneficial for the improvement of OER activity in alkaline medium, even surpassing the benchmark IrO₂ and BSCF catalysts,¹⁷ whereas nanostructured SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3- δ} shows a decent bifunctional OER/HER activity.⁶ Nevertheless the oxygen electrocatalytic activity of perovskite oxides still lag behind several other nanoheterostructures, alloys and layered double hydroxides.^{2,5,7}

The catalytic activity of perovskite oxides can be improved by *in situ* decoration of metallic NPs on their surface.¹⁸ The traditional methods of surface incorporation of NPs are wet impregnation or vapor deposition, which however offer limited control over size, distribution, anchorage of the deposited particles along with coarsening and agglomeration of the NPs at higher temperatures (\geq 700°C) leading to performance degradation.^{19,20} In case of NPs grown by traditional methods at low or room temperature, there is always a possibility of agglomeration

and detachment of NPs from the catalyst surface during long term operation at high applied potential. In situ surface immobilization of metallic NPs exsolved from the parent perovskite lattice can avoid such issues and this strategy has been applied in high-temperature solid oxide fuel cells and room temperature electrocatalytic applications.²¹⁻²⁵ Although the stability of such a surface immobilization is still not understood,¹⁹ the exsolution process is particularly facilitated from A-site vacant ABO₃ lattice.²⁶ A:B stoichiometry plays a vital role during the exsolution process. When A/B = 1, B site vacancies created by exsolution usually results in the segregation of A-site cations, leading to a decrease in the catalytic activity but in the presence of A-site deficiency (A/B < 1), A-oxides are less likely to form upon exsolution and a wider range of NP compositions with superior surface distribution and coverage can be achieved. A-site deficiency therefore serves as a general driving force to trigger B-site exsolution along with the formation of stable perovskite structure preventing the undesirable components containing A-site cation.²⁷ In spite of the advantage of creating additional catalytically active sites by surface modification with metal NPs,^{1,11} the challenge is steeper when this strategy is applied to create a NP decorated single perovskite composition with trifunctional catalytic activity for OER, ORR and HER. The chosen exsolution temperature, particle size and surface area control, optimization of eg orbital filling and rational steering of the defect chemistry thereby tuning the electronic environment are the crucial factors in governing the electrocatalytic activity.^{11,28}

Herein we exhibit a perovskite composition that can be engineered into an efficient trifunctional electrocatalyst. Starting from SrCoO₃ (SC) and SrCo_{0.9}Nb_{0.1}O_{3- δ} (SCN), Sr_{0.95}Nb_{0.1}Co_{0.9-x}Ni_xO_{3- δ} (SNCN, 0.1 $\leq x \leq 0.4$) was prepared by non-aqueous sol-gel method and then reduced in 10% H₂/N₂ atmosphere at different temperatures to create exsolved Co-Ni NPs. A uniform distribution of smaller Co-Ni NPs can be tuned at lower reduction temperatures which results in improved ORR, OER and HER activity with lower overpotentials, In turn surpassing many reported perovskite oxide catalysts. Besides the presence of bimetallic NPs on the oxide surface, the enhanced catalytic activity in alkaline medium is due to a synergism between the oxide host and exsolved NPs, B-site point defects, oxygen non-stoichiometry, optimized e_g filling, surface oxygen defects, metal-oxygen bond covalency, charge transfer resistance and effective metallicity at B-site of the perovskite.

(2)

Results and discussion

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The introduction of point defects by cation exsolution occurs through the instantaneous creation of oxygen and metal vacancies, according to step (1) in the following mechanism. The surface metal oxide thus formed is then converted to the corresponding metal under reducing atmosphere according to step (2):

$$B^{x}{}_{Co/Ni} + O_{0}^{x} \leftrightarrow BO(s) + V_{0}^{00} + V''_{Co/Ni}$$

$$\tag{1}$$

$$BO(s) \leftrightarrow B_{Metallic}(s) + \frac{1}{2}O_2(g)$$

where, $B^{x}_{Co/Ni}$ is the B-site dopant with net charge zero, O_{0}^{x} is oxygen in the lattice with net charge zero, V_{0}^{00} is the oxygen ion vacancy with net charge +2, $V''_{Co/Ni}$ is the cation vacancy at B-site with net charge -2, and *BO* is the oxide formed with B-site cation. Oxygen vacancies enable a relatively inactive catalyst surface to become reactive even at room temperature. Presence of surface oxygen vacancies accelerate the kinetics of redox reactions by reducing the energy barriers,²⁹ and moreover the initially adsorbed species gets trapped at these defect sites for conversion to new chemical entities which otherwise may diffuse along the surface.³⁰ The vacancy sites also possess weakly bound electrons which serve as Lewis base sites for adsorption of molecules and forming the intermediates, thereby making the overall reaction more efficient.³¹ Since surface co-segregation of Co, Ni, and Co-Ni accompanied by oxygen vacancy is thermodynamically favorable,^{19,32} the possibility of bimetallic NP formation on the perovskite surface becomes a feasible process. $SrNb_{0,1}Co_{0,9-x}Ni_xO_{3-\delta}$ ($0.1 \le x \le 0.4$) perovskites were obtained by calcination at 1000°C and even with A-site vacancy and partial substitution of Co by Nb and Ni, the X-ray diffraction (XRD) patterns conform to the parent $SrCoO_{3-\delta}$ according to JCPDS 39-1083 (Fig. S1a[†]).

Rietveld refined XRD patterns of $Sr_{0.95}Co_{0.8}Nb_{0.1}Ni_{0.1}O_{3-\delta}$ (S1) and $Sr_{0.95}Co_{0.7}Nb_{0.1}Ni_{0.2}O_{3-\delta}$ (S2) show their crystallization in the perovskite phase with space group *Pm-3m* (Fig. 1a and b). With increasing Ni content the (110) reflection gradually shifts to higher 20 indicating reduction in lattice volume due to the ionic radii of Ni²⁺ and high spin Co²⁺ being 0.69Å and 0.745Å, respectively (Fig. S1b†). The composition estimated by X-ray fluorescence (XRF) shows the Sr:Co:Nb:Ni ratio to be 47.7:39.7:4.8:5.1 for S1 and 46.9:35.7:4.9:9.8 for S2, which are very close to the original compositions. After reduction at 400°C in 10% H₂/N₂, both S1-400 and S2-400 retain their perovskite structure predominantly along with the formation of

impurity phases such as CoO and NbO₂ (Fig. S1c and d†). The exsolved bimetallic CoNi reflection at $2\theta = 44.3^{\circ}$ lies in between Co (JCPDS 15-0806) and Ni (JCPDS 04-0850).



Fig. 1 Rietveld refined XRD patterns of (a) S1, (b) S2, (c) S1-400 and (d) S2-400. Schematic representations of (e) structural transformation and (f) surface morphology evolution of S2 to S2-400 under reducing atmosphere. The symbols are: perovskite (o), NbO₂ (#), CoO (^), CoNi (•) and unknown phase (+).

With the rise in reduction temperature up to 900°C, the perovskite structure starts to degrade more along with the formation of higher amount of impurity phases. Surface localization of the NPs results in Schottky type defects and oxygen vacancies within the perovskite lattice, because of which the repulsive force between neighboring cations expands the lattice observed from a downshift of the (110) reflection (Fig. S1e and f⁺).²¹ The oxygen nonstoichiometry (δ) is found to be 0.22, 0.28, 0.33, and 0.39 for S1, S2, S1-400, and S2-400, respectively (Discussion S1 and Table S1[†]). In S1-400 and S2-400, while the perovskite phase in the XRD patterns were refined against $SrCo_{0.5}Nb_{0.5}O_3$ (Crystallography Open Database, COD 1522293), the reflections of bimetallic CoNi NPs were matched with $Co_{0.75}Ni_{0.25}$ (COD 1525374) and the impurity phases were refined against CoO (COD 1533087) and NbO₂ (COD 1548821) (Fig. 1c and d). In S1-400 and S2-400, the B-site point defects weaken the hybridization strength between B-site metal and O, because of which the B-O bond length increases (Table 1).³³ Although exsolution maintains an intact perovskite lattice there are local changes in electronic environment around the B-site cation due to introduction of point defects, accompanied by surface localization of bimetallic NPs and metal oxide impurities of NbO₂ and CoO, schematically represented in Fig. 1e and f.

Table 1. Rietveld refinement data.

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| Sample | A | Volume (Å ³) | χ^2 | R _{wp} | B-O (Å) |
|--------|--------|--------------------------|----------|-----------------|---------|
| S1 | 3.8762 | 58.239 | 0.93 | 2.18 | 1.938 |
| S2 | 3.8699 | 57.956 | 1.75 | 3.55 | 1.935 |
| S1-400 | 3.8902 | 58.873 | 2.61 | 5.74 | 1.945 |
| S2-400 | 3.9042 | 59.511 | 2.37 | 4.18 | 1.952 |



Fig. 2 Low and high resolution TEM images with SAED patterns of (a) S1, (b) S2 (c) S1-400 and (d) S2-400. The legible heterojunction between exsolved CoNi and the perovskite host is shown in (c) and (d).

High temperature reduction in 10% H₂/N₂ changes the agglomerated clusters of parent perovskite oxides (Fig. S2[†]) to exsolved 15-80 nm NPs uniformly distributed on the perovskite oxide surface (Fig. S3 and Fig. S4⁺). Exsolution at 400-500°C maintains the surface localized NP size to 15-30 nm, ideal for maintaining the catalytically active sites. Transmission electron microscopy (TEM) images in Fig. 2 show the anisotropic morphology of the perovskite oxide particles. The lattice spacing of 0.27 nm matches well with (110) reflection and selected area electron diffraction (SAED) patterns with the (110), (111), (210), (211) and (220) diffraction spots of cubic perovskite lattice validate the crystallinity of the particles. In S1-400 and S2-400, the surface localization of the <30 nm NPs on the perovskite surface is clearly visible (Fig. 2c and d^{\dagger}), with a crystalline hetero-junction between the perovskite backbone and exsolved NP. The measured *d*-spacing can be assigned to (110) plane of SNCN perovskite (0.27 nm) and (111) plane of CoNi bimetallic NP (0.21 nm). The bimetallic nature of the exsolved NPs is validated from the high-angle annular dark-field scanning TEM (HAADF-STEM) imaging coupled to energy-dispersive X-ray spectral (EDS) mapping in Fig. 3 where only Co and Ni are observed on the NPs in comparison to the perovskite backbone where all the elements are uniformly distributed. The perovskite backbone after high temperature reduction strongly resembles the elemental maps of S1 and S2, before reduction (Fig. S5⁺). Oxygen signal is absent on the exsolved NPs, further strengthening the claim of their composition to be Co-Ni. When the reduction was performed at a higher temperature such as 900°C, the diameter of the exsolved NPs expectedly increases to 50-80 nm (Fig. S6[†]). The surface segregation of the Co-Ni NPs was also cross-checked from atomic force microscopy (AFM) where ~ 20 nm NPs are observed to be uniformly distributed on the perovskite surface (Fig. S7⁺).

The oxidation states of the elements were elucidated from the X-ray photoelectron spectral (XPS) analyses (Fig. 4, Fig. S8, Fig. S9 and Table S2 and S3[†]). Between different perovskite oxide compositions, S1 and S2, no significant change in the binding energies of Sr *3d* and Nd *3d* levels is observed (Fig. S8[†]). The O *Is* spectra are deconvoluted to four characteristic peaks of lattice oxygen species, O²⁻ (529.6 eV), highly oxidative species, O²⁻/O⁻ (530.5 eV), hydroxyl groups or the surface adsorbed oxygen, -OH/O₂ (531.2 eV) and adsorbed molecular water (532.5 eV) (Fig. S9[†]).^{6,13} From the area of fitted peaks, the relative content of O₂^{2-/O⁻} species is found to be higher in S1 than S2, which has direct correlation with the catalytic activity of the perovskites.⁶ The oxidation states of the catalytically active B-site cations are of

most significance here (Fig. 4). The Co $2p_{3/2}$ and $2p_{1/2}$ doublets at 780.42 and 795.60 eV for S1, and 780.23 and 795.45 eV for S2, respectively are deconvoluted into three peaks corresponding to Co³⁺, Co²⁺ and Co satellite. From the relative peak area, the average cobalt oxidation state is calculated to be 2.60 and 2.45 for S1 and S2, respectively.



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Fig. 3 STEM-HAADF images and elemental mapping of (a) S1-400 and (b) S2-400, showing the exclusive presence of Co and Ni in the exsolved NPs.

Similarly the Ni $2p_{3/2}$ and $2p_{1/2}$ peaks observed at 855.71 and 872.19 eV for S1, and 855.55 and 872.73 eV for S2, respectively are deconvoluted into Ni³⁺, Ni^{2+,} and Ni satellite. The average oxidation state of Ni is found to be 2.34 and 2.20 in S1 and S2, respectively. Considering Co³⁺ in intermediate-spin state, Co²⁺ in the high-spin state and Ni³⁺ as low-spin, the e_g orbital filling is 1.23 and 1.37 for S1 and S2, respectively, close to the reported best e_g occupancy of 1.0 for ORR and 1.2 for OER.^{28,34} Due to bimetallic NP segregation at the perovskite oxide surface, S1-400 and S2-400 also have metallic Co⁰ and Ni⁰ states observed at 778 and 852.40 eV, respectively. The spectral broadness is due to the presence of multiple species which results in multiplet splitting of conduction electrons and shake-up phenomena,

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and/or intra-and inter-band transitions allowed by breakdown of dipole selection rules in polycrystalline samples with delocalized electrons.³⁵



Fig. 4 XPS spectra of Co 2p level in (a) S1 and (b) S1-400; Ni 2p level in (c) S1 and (d) S1-400; Co 2p level in (e) S2 and (f) S2-400; Ni 2p level in (g) S2 and (h) S2-400.

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Fig. 5 (a) LSV polarization curves for OER, (b) required overpotentials to achieve 10 mA cm⁻², (c) Tafel plots of the perovskite oxides with different compositions. (d) Nyquist plots obtained at 1.6 V versus RHE for OER. Inset shows the equivalent circuit. (e) Chronoamperometric durability test of S1 and S1-400. Inset shows the LSV curves of S1 before and after the durability test. (f) Faradaic efficiency of S1 showing the theoretically calculated and experimentally measured O₂ gas with time at -1.7 V versus RHE. (g) OER polarization curves of differently reduced S1 and (h) their required overpotentials to achieve 10 mA cm⁻².

The above characterization details have direct implications on the electrocatalytic activities of the SNCN catalysts before and after reduction. Fig. 5a shows the linear sweep voltammogram (LSV) curves demonstrating OER activity of the catalysts mixed with 10 wt% conducting carbon black. Both carbon paper (CP) and conducting carbon powder (CCP) show negligible activity validating no significant role of the electrodes themselves. S1 shows an onset potential of 1.55 V which is little higher compared to state-of-the-art OER catalysts including IrO₂.^{17,36} S1 catalyst shows the lowest overpotential (η_{10}) of 438 mV while all other catalysts in the series show lesser performance (Fig. 5b). The activity trend draws a direct correspondence to the e_g orbital filling and O₂^{2-/O-} ratios, discussed earlier. The Tafel slope of S1 is found to be 64 mV dec⁻¹ (Fig. 5c and Table S4†) which is lower than that other reported catalysts like Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- $\delta}$} (94 mV dec⁻¹), SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3- δ} (76 mV dec⁻¹),¹⁷ Pr_{0.5}Ba_{0.5}CoO_{3- δ} (82 mV dec⁻¹),³⁶ and LaNiO_{3- δ} (95 mV dec⁻¹),³⁷ indicating superior kinetics of S1 (Table S5†).³⁸⁻⁶⁰ Nyquist plots reveal the least charge transfer resistance for S1 (Fig. 5d). The best performing catalyst, S1 shows excellent stability for at least 100 h at a constant potential of 1.68 V (vs. RHE) to achieve a current density of 20 mA cm⁻² (Fig. 5e). The catalyst morphology remains

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intact after 100 h demonstrating its suitability for long-term operation (Fig. S10⁺). The faradic efficiency of OER measured by eudiometry is 96% revealing maximum consumption of charge and absence of any side reaction (Fig. 5f). Among the reduced samples containing exsolved NPs, S1-400 shows the best OER activity with an onset potential 1.5 V and overpotential of 380 mV to achieve a current density of 10 mA cm⁻² (Fig. 5g and h). The decrease in η_{10} by 58 mV from S1 to S1-400 without compromising the 100 h stability (Fig. 5e) owes to the creation of point defects by introducing cation vacancies at the catalytically active B-site of perovskite oxide lattice, and enhanced electrochemically active surface area (ECSA). ECSA is directly proportional to the electrochemical double-layer capacitance (C_{dl}) which is 8, 5, 13 and 11 mF for S1, S2, S1-400 and S2-400, respectively (Fig. S11⁺), highlighting the significance of exposing more active sites by exsolution. Furthermore, the intrinsic property of the OER catalyst is revealed by another figure-of-merit, the turnover frequency (TOF), which is 0.11 s⁻¹ for S1-400 larger than 0.03 s⁻¹ for S2-400 at 300 mV overpotential (Discussion S2⁺). With further rise in reduction temperature from 400 to 900°C, η_{10} increases since the perovskite structure starts to disintegrate (Fig. 1) accompanied by the exsolved NP diameter (Fig. S3⁺). The lowest OER overpotential that of S1-400 is in fact lower or comparable to other literature reported perovskite oxide catalysts (Table S5[†]).



Fig. 6 (a) LSV polarization curves for ORR at 1600 rpm, (b) required overpotentials to achieve - 3 mA cm^{-2} , (c) Tafel plots of the perovskite oxides with different compositions. (d) Nyquist plots obtained at 0.5 V versus RHE for ORR at 1600 rpm. Inset shows the equivalent circuit. (e) LSV polarization curves for ORR of S1 at different rpm. (f) Chronoamperometric durability test of S1 and S1-400. Inset shows the LSV curves of S1 before and after the durability test. (g) ORR polarization curves of differently reduced S1 and (h) their required overpotentials to achieve -3 mA cm⁻².

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The electronic structure dependent ORR performance measured by rotating disc electrode (RDE) in O₂-saturated 1 M KOH solution is evident from the LSV plots recorded at a rotation speed of 1600 rpm (Fig. 6a). As expected, Pt/C shows the best ORR performance while CP and CCP show negligible activity. Here too S1 shows the best ORR activity in the series with an onset potential of 0.97 V (Fig. S12⁺) and a limiting current density of -6.2 mA cm⁻². The overpotential to reach a current density of -3 mA cm⁻² is found to be minimum for S1 (395 mV, Fig. 6b) and this activity is superior or comparable to several perovskite oxides reported in the literature (Table S5[†]).^{12,38-63} S1 also shows more positive half-wave potential as compared to rest of the compositions viz. 0.87 V for S1, 0.82 V for S2, 0.75 V for S3 and 0.65 V for S4 versus RHE. In the control cyclic voltammetry (CV) experiments with S1, there has been no oxidation/reduction feature in N2 saturated solution in 1 M KOH at 10 mV s⁻¹ however a small ORR peak appears in O2 saturated medium at 0 rpm (Fig. S13[†]). At 1600 rpm in O2 saturated KOH medium, the current increases which is consistent with previous reports confirming high ORR activity of S1 (Table S5[†]). S1 also shows a Tafel slope of only 90 mV dec⁻¹ (Fig. 6c and Table S4[†]) and lower electron-transfer resistance (Fig. 6d). At different rotations, 0-2800 rpm, the current changes from a transient behavior to steady state curve, demonstrating positive relationship of the limiting current density with rotation speed (Fig. 6e). The chronoamperometric test at 483 mV versus RHE reveals no loss in current density even after 10h operation (Fig. 6f) and the LSV curves measured at 1600 rpm before and after the stability test show no significant change indicating superior stability of S1 catalyst (Fig. 6f inset) also retaining its morphology intact (Fig. S14⁺). Similar to OER, the ORR performance of S1-400 is the best among the reduced samples, with an overall decrease in overpotential at -3 mA cm⁻² from S1 to S1-400 by 48 mV (Fig. 6g and h). The synergistic contribution of the exsolved NPs and host perovskite along with the surface oxygen defects, optimized e_g filling and lower metaloxygen bond hybridization result in improved ORR activity of S1-400.23 The presence of catalytically inactive NbO2 on the perovskite oxide surface is thereby surpassed by the active bimetallic Co-Ni NPs.

The remaining last part of the trifunctional activity of these perovskite catalysts is HER and herein S2 shows better activity than S1 considering the η_{-10} values (Fig. 7a and b). While by Nb doping, η_{-10} decreases from SC (447 mV) to SCN (427 mV), the B-site Ni-doping further decreases η_{-10} from S1 (340 mV) to S2 (299 mV). An excess of Ni doping as in S3 and S4

however does not help. The effective metallicity and optimized oxygen vacancy concentration boost the HER activity of S2, which is better than BSCF ($\eta_{10} = 342 \text{ mV}$),¹³ and several other bulk or nanostructured perovskite / non-perovskite electrocatalysts (Table S6†).^{13,64-73}



Fig. 7 (a) LSV polarization curves for HER, (b) required overpotentials to achieve -10 mA cm⁻², (c) Tafel plots of the perovskite oxides with different compositions. (d) Nyquist plots obtained at -0.4 V versus RHE for HER. Inset shows the equivalent circuit. (e) Chronoamperometric durability test of S2 and S2-400. Inset shows the LSV curves of S2 before and after the durability test. (f) Faradaic efficiency of S2 showing the theoretically calculated and experimentally measured H₂ gas with time at -0.4 V versus RHE. (g) HER polarization curves of differently reduced S2 and (h) their required overpotentials to achieve -10 mA cm⁻².

The Tafel slopes obtained from the Tafel plots (Fig. 7c) are however the lowest for S1 (64 mV dec⁻¹) than for S2 (80 mV dec⁻¹) (Table S4†). In fact the slopes do not match with the limiting values of 120, 40 or 30 mV dec⁻¹ applicable for the Volmer, Heyrovsky or Tafel processes, respectively.¹³ Therefore ambiguities exist regarding the HER mechanism which generally involves the Volmer process (electrochemical hydrogen adsorption) followed by either the Heyrovsky process (electrochemical desorption) or Tafel process (chemical desorption).⁷⁴ S2 has the fastest charge transfer kinetics (Fig. 7d) and very good stability tested for 100h at a constant potential of 357 mV (Fig. 7e and Fig. S15†). S2 also shows a faradaic efficiency of 97.4% demonstrating its high energy conversion efficiency (Fig. 7f). Among the reduced samples, the best performing S2-400 works at $\eta_{-10} = 208$ mV, a remarkable drop of $\Delta\eta_{-10}$ by 91 mV from S2 to S2-400 (Fig. 7g and h). The better HER performance of S2 and S2-400 than S1 and S1-400,

respectively is evidently due to higher Ni content in the former two, since Ni serves as the active site because of its lower Gibbs free energy of H* adsorption.² In a perfect synergy in S2-400, an intact perovskite host lattice albeit with lower metal-oxygen hybridization aids the dissociation of water whereas the exsolved NPs assist in hydrogen adsorption.²⁵ The TOF of S2-400 for HER is found to be higher (2.08 H₂ s⁻¹) than S1-400 (0.66 H₂ s⁻¹, Discussion S2†). S2-400 also shows constant HER activity during a 100 h long run (Fig. 7e). Post OER and HER 100 h stability experiments, XRD patterns remain similar to those before catalysis, confirming the long-term phase stability under OER and HER conditions (Fig. S16†). In fact S2-400 is a pH universal HER catalyst wherein at pH 0, η_{-10} is only 183 mV (Fig. S17†), lower than that at pH 14, since reduction of H⁺ to H* is more facile than H₂O to H*. Because of the outstanding capability of reduced samples in catalyzing OER and HER, an electrolyzer with two electrode configuration using S1-400 and S2-400, both deposited on carbon paper, as anode and cathode, respectively was constructed for overall water electrolysis. The S1-400 || S2-400 electrolyzer delivers a current density of 10 mA cm⁻² at a cell voltage of 1.81 V in 1 M KOH solution with continuous release of gas bubbles (Fig. S18†).

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OER and HER electrochemical measurements of the best performing catalysts, S1-400 and S2-400, were also carried out in 0.1 M KOH for effective comparison with the literature. Due to lower ionic conductivity of the electrolyte in dilute alkaline solution, catalyzing the OER and HER processes become slightly more strenuous, in spite of which these catalysts exhibit prominent activity. The required overpotential for S1-400 becomes 429 mV for OER and S2-400 shows overpotential of 274 mV for HER (Fig. S19†). In case of ORR, the trend is reversed as compared to 1 M KOH because the oxygen solubility increases with decrease in KOH concentration (Fig. S20a†). S1-400 also shows more positive half-wave potential of 0.92 V in 0.1 M KOH compared to 0.87 V versus RHE in 1 M KOH. The overpotential to reach a current density of -3 mA cm⁻² is found to be 293 mV for S1-400 in 0.1 M KOH (Fig. S20b†). The ORR onset potential of S1-400 also shifts to more positive value from 0.97 V in 1 M KOH to 0.98 V in 0.1 M KOH along with the increase in current density. For quantitative evaluation of the ORR activity of S1-400, the RRDE technique has been employed to obtain kinetic information in O₂-saturated 0.1 M KOH solution. Fig. S20c† shows the disk and ring currents collected on a rotated S1-400 electrode at 1600 rpm. The RRDE test shows a quasi-four-electron transfer process

(above 3.9) in the potential range of 0.6-0.9 V and the yield of H_2O_2 is below 2% (Fig. S20d[†]), demonstrating the desired ORR activity of S1-400.

In alkaline medium, the overall HER process consists of adsorption of H₂O molecules and their reduction to form H_{ads} and OH⁻, adsorption and desorption OH⁻ and formation of H_{ads} for H₂ evolution (Fig. S21⁺).⁷⁵ OER generally proceeds through the adsorption of OH⁻ on to the active sites, followed by four electron transfer steps involving a series of intermediates like HO*, O*, and HOO* along with the redox of B-site cation.^{6,76} In ORR, the undissolved oxygen molecule adsorbs directly on the active sites according to the inner-sphere mechanism, whereas in case of outer-sphere mechanism, the surface adsorbs hydroxide ions and oxygen molecules are solvated.⁷⁷ Here too the 4e⁻ process is associated with the change in valence state of the transition metal where O-O bond cleaves to produce O* and OOH* intermediates, and B^{(m+1)+}-O²⁻ is formed by electron transfer from the metal site to the O* intermediate.³⁴ The activity of best performing catalysts were also measured without adding 10 wt% conducting carbon black (Figure S22[†]). As expected the OER, ORR and HER overpotentials slightly increase in the absence of synergistic interfacial interaction between perovskite and carbon. The OER and ORR overpotentials of S1-400 increase by 20 and 23 mV, respectively while the HER overpotential of S2-400 increases by 11 mV. Besides enhancing electronic conductivity of the electrode, the above results suggest a more complex role of carbon black, understanding the mechanism of which needs detailed future studies. The perovskite-carbon interface likely changes the local electronic environment of the perovskite which attunes the catalytic performance.⁷⁸

Although the detailed mechanistic understanding of these reactions on perovskite oxide surface is still limited, we have attempted elucidating the participating radicals across the potential range of measurement, by employing scavengers for specific radical intermediates in case of ORR only, since in the potential window of OER, the scavengers get oxidized.⁷⁹ In the present study KI, p-benzoquinone and sodium azide are selected as OH*, O₂-, and OOH* radical scavengers, respectively and the corresponding processes are shown in Fig. 8a and c.⁸⁰ Adding a scavenger at different potentials decreases the abundance of that particular radical and if the radical plays a prominent role in that potential range, the current will also drop (Fig. S23†). The effect of KI is more prominent at lower potentials, -0.1 and -0.4 V, while the scavenging by p-benzoquinone and sodium azide is effective in the higher potential range, here -0.6 V. Observing

the drop in current by these three scavengers (Fig. 8d and f), OH* is predominant in the entire potential range whereas O_2^{-} , and OOH* play major role at higher potentials.



Fig. 8 Schematic representation of the radical scavenging reactions by (a) KI, (b) pbenzoquinone and (c) NaN_3 , and the corresponding drop in current at different potentials due to addition of the scavengers, (d) KI, (e) p-benzoquinone, and (f) NaN_3 .

Conclusions

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In summary, we demonstrated the design of trifunctional perovskite oxide catalysts by creating oxygen vacancies and point defects by NP exsolution, and reduced B-site metal – oxygen hybridization. $Sr_{0.95}Nb_{0.1}Co_{0.9-x}Ni_xO_{3-\delta}$ (SNCN, $0.1 \le x \le 0.4$) systems were prepared by the nonaqueous sol-gel route and calcined at 1000°C. The oxygen vacancies and point defects were created through exsolution of B-site metals and their uniform surface localization in the form of <30 nm Co-Ni bimetallic NPs by reducing the perovskite oxides in 10% H₂/N₂ at different temperatures. 400°C was observed to be the most suitable reducing temperature since at higher temperatures, the perovskite oxide structure was found to disintegrate. Although when x = 0.1, both OER and ORR activity improved, whereas HER is more facilitated by x = 0.2. The utility of the exsolution process is the remarkable drop in overpotential by 58, 48 and 91 mV at 10 mA cm⁻², -3 mA cm⁻² and -10 mA cm⁻² for OER, ORR and HER, respectively at pH 14 as compared to the preceding parent perovskites. In case of ORR, the radical intermediates O₂⁻, and

OOH* are more active at higher potentials whereas OH* is prevalently active over the entire potential range. The best HER catalyst is pH universal such that the overpotential drops to 183 mV at pH 0. The obtained hybrid catalysts exhibited excellent ORR/OER/HER activity and durability in alkaline solution, comparable or even better than many reported perovskite oxide and non-perovskite based catalysts. The modulation of several factors such as optimal e_g orbital filling, metal-oxygen bond hybridization, oxygen non-stoichiometry, surface oxygen vacancies, good ionic and charge-transfer abilities, the synergistic effect of bimetallic NP and perovskite oxide pave the way for achieving this rare class of trifunctional electrocatalysts based on perovskite oxide.

Experimental section

Materials

For the synthesis of SrCoO₃, SrCo_{0.9}Nb_{0.1}O_{3- δ}, Sr_{0.95}Co_{0.9-x}Nb_{0.1}Ni_xO_{3- δ} (*x* = 0.1-0.4) catalysts, strontium (II) nitrate (Alfa Aesar, 99%), cobalt (II) nitrate hexahydrate (Merck, \geq 98%), nickel (II) nitrate hexahydrate (Merck, \geq 97%), niobium (V) oxalate hydrate (Alfa Aesar), and ethylene glycol (Merck, \geq 99%) were used. For electrochemical measurements Toray carbon paper (Alfa Aesar), nafion (Sigma Aldrich, 5 wt%), carbon black (Alfa Aesar, Super P conductive, 99+%), and potassium hydroxide (Merck, \geq 85%), were used along with double distilled water. In the present work, all the chemicals were used without further purification.

Synthesis of the catalysts

SrCoO₃ (SC), SrCo_{0.9}Nb_{0.1}O_{3-δ} (SCN), Sr_{0.95}Co_{0.9}Nb_{0.1}O_{3-δ} (S95CN), Sr_{0.95}Co_{0.8}Nb_{0.1}Ni_{0.1}O_{3-δ} (S1), Sr_{0.95}Co_{0.7}Nb_{0.1}Ni_{0.2}O_{3-δ} (S2), Sr_{0.95}Co_{0.6}Nb_{0.1}Ni_{0.3}O_{3-δ} (S3), Sr_{0.95}Co_{0.5}Nb_{0.1}Ni_{0.4}O_{3-δ} (S4) were synthesized following our previously reported nonaqueous sol-gel method.⁸ Stoichiometric amounts of metal salts corresponding to a particular composition were dissolved one by one in 40 ml ethylene glycol under continuous stirring at 80°C for 1h. The obtained clear solution was refluxed for 12h at 120°C. Then the dark brown colored solution was transferred into a beaker and heated at 120°C to obtain a dry black powder. The powder was ground by mortar-pestle and calcined in an alumina boat at the center of a tube furnace (Thermo SCIENTIFIC, model: STF55433PC-1) at 1000°C for 10h in air with 5°C/min heating rate to obtain single phase perovskite oxides.

NP exsolution – creation of point defects

Physicochemical characterization

The samples were characterized by room temperature powder XRD by Rigaku mini flex II with Cu K α radiation ($\lambda = 1.54059$ Å) operated at a tube voltage of 40 kV and a current of 40 mA with scan speed $2\theta = 1^{\circ}$ /min in the 2 θ range 20-80°. Rietveld refinement of the XRD patterns was performed by General Structure Analysis System (GSAS) software (Los Alamos National Laboratory Report, 2004). Oxygen nonstoichiometry of best-performing compositions was analyzed by thermogravimetric analysis.¹¹ The composition of calcined powders was determined by X-ray fluorescence instrument (S8 Tiger from Bruker-AXS, Germany). The morphology of the calcined and reduced powders was obtained by field-emission scanning electron microscopy (FESEM, Carl Zeiss SUPRA 55VP). TEM images were recorded with the DST-FIST TEM facility of IISER Kolkata, model UHR-FEG-TEM, JEOL, JEM 2100 F operating at 200 kV. HAADF-STEM and the corresponding EDS mapping were recorded by the same instrument. Surface topology of the 400°C reduced samples was studied by AFM using NT-MDT Nova AFM. Elemental oxidation states at the NP surface were determined by XPS using PHI 5000 Versaprobe II, FEI Inc. and the data fitted by Fityk 0.9.8 software.

Electrode preparation

Working electrodes for OER and HER measurements were prepared by drop casting the catalyst ink on carbon paper. The catalyst ink was prepared by dispersing 3 mg powder in 500 μ l of 1:1 ethanol:water mixture followed by addition of 10 μ l of 5% Nafion and 0.3 mg conducting carbon. For uniform dispersion, the mixture was bath sonicated for 30 min. The prepared ink was then uniformly drop-casted on carbon paper of geometric area ~0.3 cm² with a loading of 1 mg/cm². The working electrode for ORR measurement was prepared by controlled drop-casting of the catalyst ink on a rotating disc electrode (RDE) made of glassy carbon (0.07 cm², ALS Japan). Before use, the RDE was polished using aqueous alumina suspension and sonicated in ethanol. The RDE was finally rinsed with distilled water. All the working electrodes were dried properly in air before each measurement.

Electrochemical measurements

OER and HER electrochemical measurements were performed in a customized three-neck glass cell with a conventional three-electrode configuration controlled by a two-channel electrochemical workstation from BioLogic Scientific Instruments, VSP300. Catalyst loaded carbon paper was used as the working electrode, Pt rod as counter electrode, Ag/AgCl in 3 M KCl as reference electrode and 1 M KOH was used as electrolyte. The catalyst mass loading was fixed at 1 mg cm⁻². The polarization curves for HER and OER were obtained from LSV measurements at a scan rate of 5 mV s⁻¹. The working electrode was prepared by drop-casting catalyst ink containing perovskite oxide and carbon black (10 wt%) on a carbon paper. The carbon black is mainly used to eliminate limitations regarding electronic conductivity and ensure full utilization of the perovskite catalyst. LSV measurements were also carried out with commercial 20 wt% Pt/C catalyst (Sigma-Aldrich), IrO₂ (Sigma-Aldrich), carbon paper (CP, Toray carbon fiber paper, Alfa Aesar) and carbon paper drop cast with conducting carbon powder (CCP) for comparison. All applied potentials were referenced to a reversible hydrogen electrode (RHE) using the equation $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E_{Ag/AgCl}^{\circ}$ and reported after *iR* correction to eliminate charge compensation due to solvent resistance using the following equation:

$$E_{iR-corrected} = E_{applied} - iR_{u}$$

where, i is the current on the electrode and R_u is the uncompensated resistance.

ORR measurements were carried out in 1 M KOH electrolyte using a three-electrode setup where the catalyst coated glassy carbon RDE was used as working electrode, Pt wire as counter electrode and Ag/AgCl in 3 M KCl as reference electrode. The working electrodes consist of the catalysts mixed with carbon black (10%) to enhance the electrical conductivity and Nafion (5 wt%, Sigma-Aldrich) acting as the binder onto glassy carbon RDE. Before each experiment, pure oxygen gas (99.9%) was purged for 1 h to make the electrolyte saturated with oxygen. During the measurements the RDE was continuously rotated at 1600 rpm to remove bubbles. LSV measurements at different rpm were also carried out. Before measuring the LSV plots, normal CV scan of 50 cycles was performed to confirm the removal of surface impurities. Tafel plots were obtained by plotting overpotential as a function of the logarithmic value of obtained current density. ECSA was calculated in the non-Faradaic zone (0-0.05 V vs. RHE) by measuring the double layer capacitance of the electrochemically active surface by CV plots. The slope, measured from the current at same potential with different scan rates denotes capacitance of the

(3)

active surface (C_s), and ECSA is the ratio of C_s to the specific capacitance for the standard oxide surface (C_o).¹¹ Electrochemical impedance spectra were measured in the frequency range from 10 mHz to 1 MHz. Chronoamperometric stability tests were performed at constant potentials depending upon the process. Faradaic efficiencies were calculated using eudiometric gas collection techniques.

ASSOCIATED CONTENT

Supporting Information

XRD patterns, FESEM images and elemental mapping of differently calcined and reduced samples, Calculation of oxygen non-stoichiometry, AFM images, XPS spectra of Sr *3d*, Nb *3d* and O *1s*, Tables showing XPS parameters and Tafel slopes, Literature comparison of OER, ORR and HER activities, FESEM images of catalysts after electrochemical stability tests, ECSA plots, TOF calculation, ORR onset potential, ORR plots of S1 under different conditions, pH universal HER activity, Electrocatalysis in dilute alkaline medium, Overall water splitting, Mechanism of electrocatalysis, LSV plots for ORR with radical scavengers.

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