Supporting Information

Title

Correlation between oxygen evolution reaction activity and surface compositional evolution in epitaxial $La_{0.5}Sr_{0.5}Ni_{1-x}Fe_xO_{3-\delta}$ thin films

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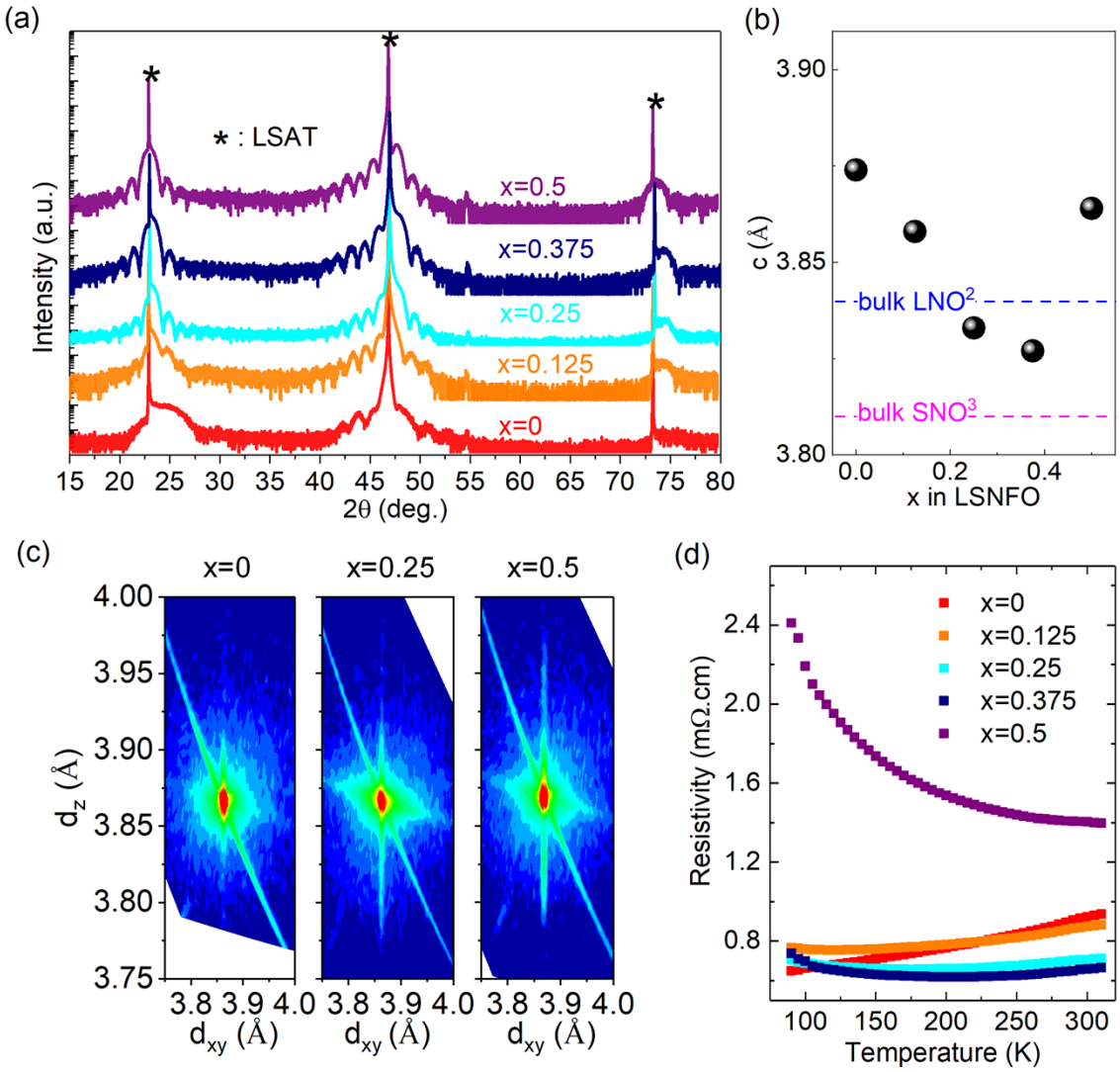

Fig. S1: (a) Extended XRD θ-2θ scans for $La_{0.5}Sr_{0.5}Ni_{1-x}Fe_xO_{3-\delta}$ (LSNFO) solid solution epitaxial films grown on LSAT. The peak near 55° in the XRD scans originates from our XRD setup.[1] (b) Reciprocal space maps for LSNFO films confirm structural coherence. (c) Out-of-plane lattice parameter (*c*) as a function of Fe content (x) in LSNFO. The blue and purple dashed lines denote the pseudo-cubic lattice constants for bulk LNO and bulk SrNiO3,[2, 3] based on which the pseudo-cubic lattice constant of bulk $La_{0.5}Sr_{0.5}NiO_3$ should be ~3.825 Å, which is smaller than that (3.868 Å) of the LSAT substrate. Hence, c for the x = 0 film is expected to be smaller than the bulk value (3.825 Å). With Fe doping, c for x > 0 films is expected to be larger than that of the x = 0 film due to the larger pseudo-cubic lattice constant (~3.883 Å)[4] of bulk $La_{0.5}Sr_{0.5}FeO_3$ compared to bulk $La_{0.5}Sr_{0.5}NiO_3$. However, experimentally we observed larger value c (~3.875 Å) for the x = 0 film and the decrease of c with increasing x from 0.125 to 0.375, suggesting that these solid solution samples may contain non-negligible amounts of oxygen vacancies. (d) Resistivity versus temperature curves for LSNFO films on heating.

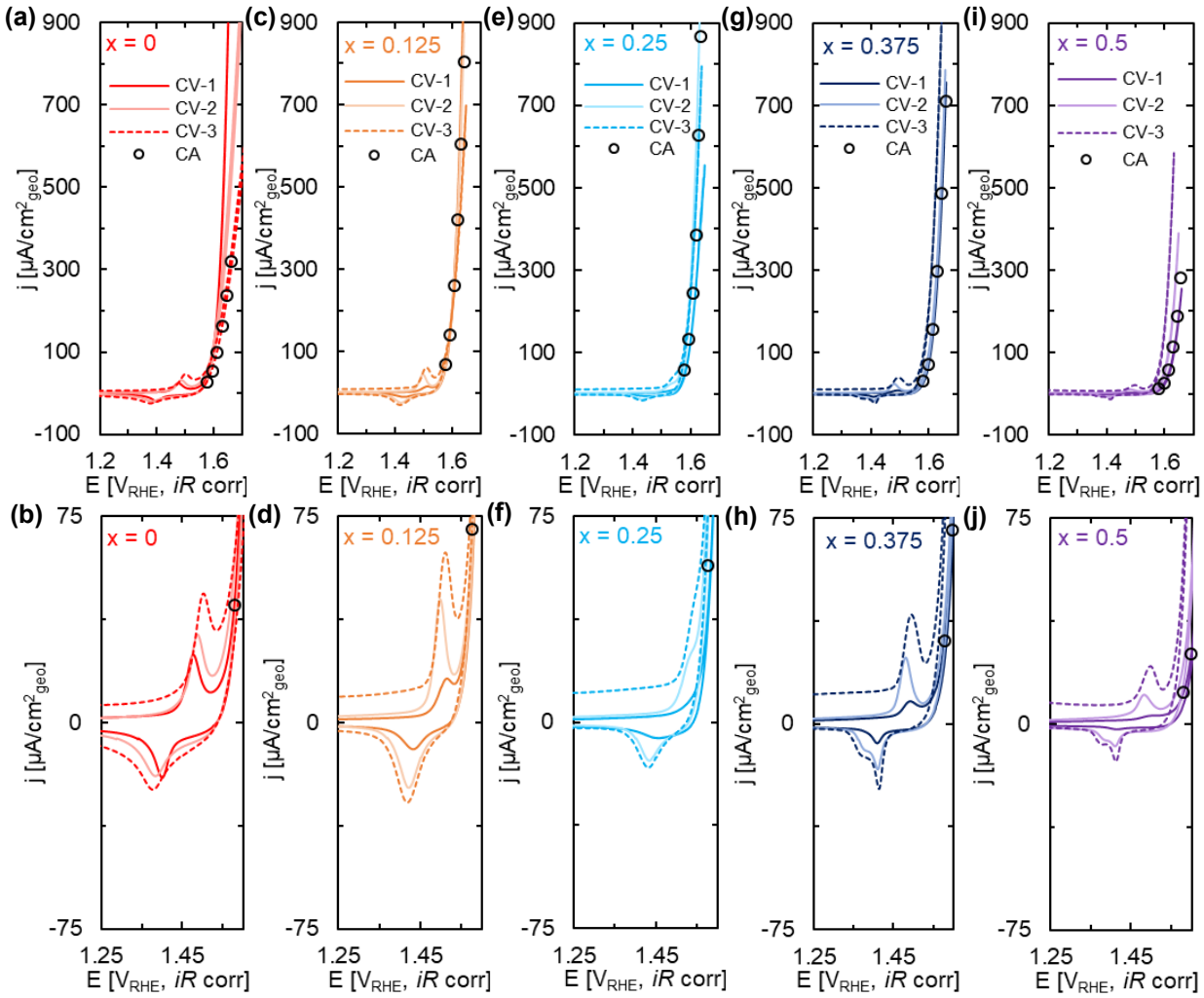

Fig. S2: (a-e) Cyclic voltammetry (CV) and chronoamperometric (CA) measurements for LSNFO films show time-dependent activity changes. The redox peaks for x ≥ 0.375 show secondary Ni reduction peak indicative of a secondary Ni phase.

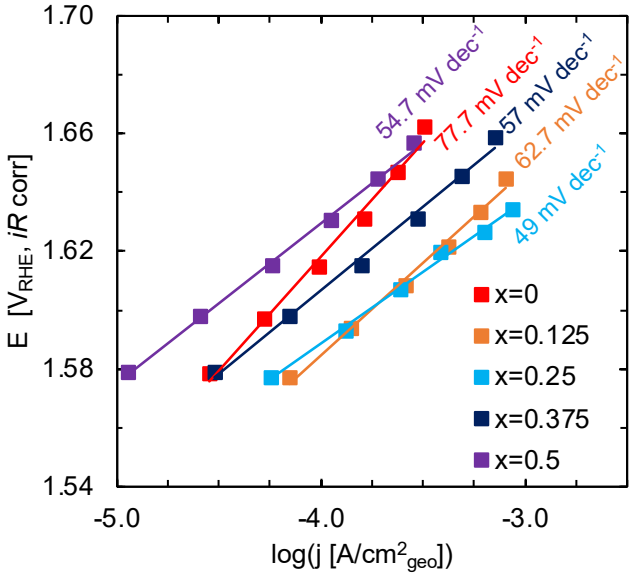

Fig. S3: Tafel slopes for LSNFO.

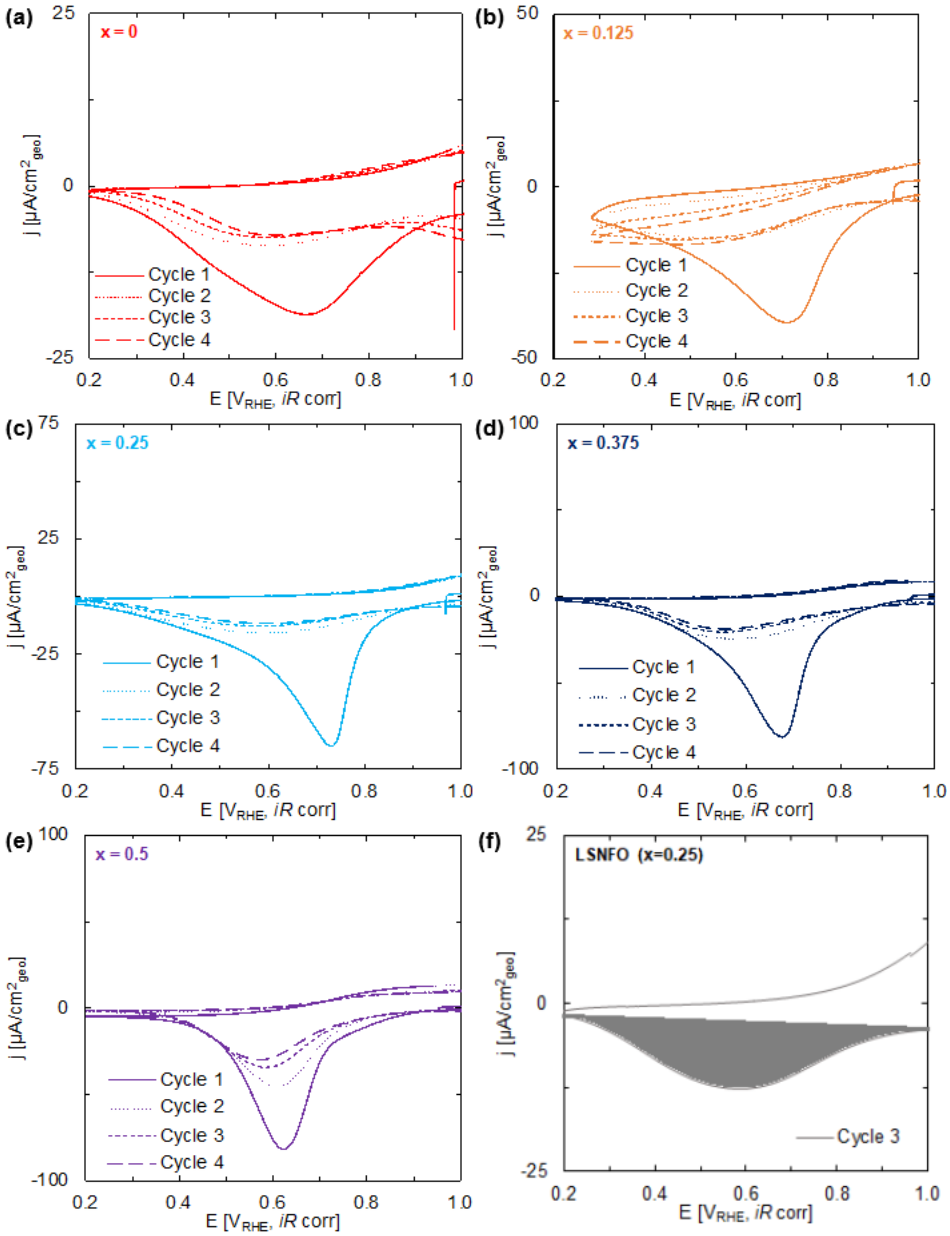

Fig. S4: (a-e) Fe reduction region of CV-3 for compositions x = 0 – 0.5, and decreasing magnitude of charge associated with Fe reduction with cycle number. (f) Example of the integrated reduction peak, multiplied by the sweep rate (10 mV/s) to estimate the reduction charge for Fe.

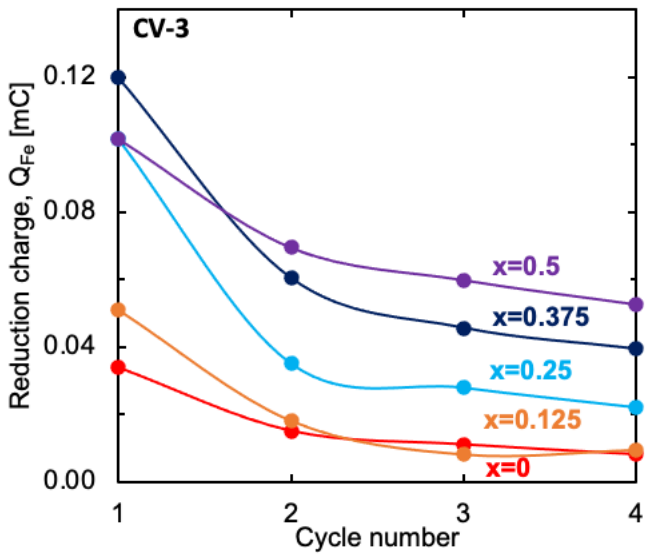

Fig S5: Dynamic changes in the Fe reduction charge indicates dynamic nature of Fe adsorption from trace Fe species in the solution.[5] In contrast, Ni reduction charge generally increased with cycling during CV-3 (inset of Figure 3b).

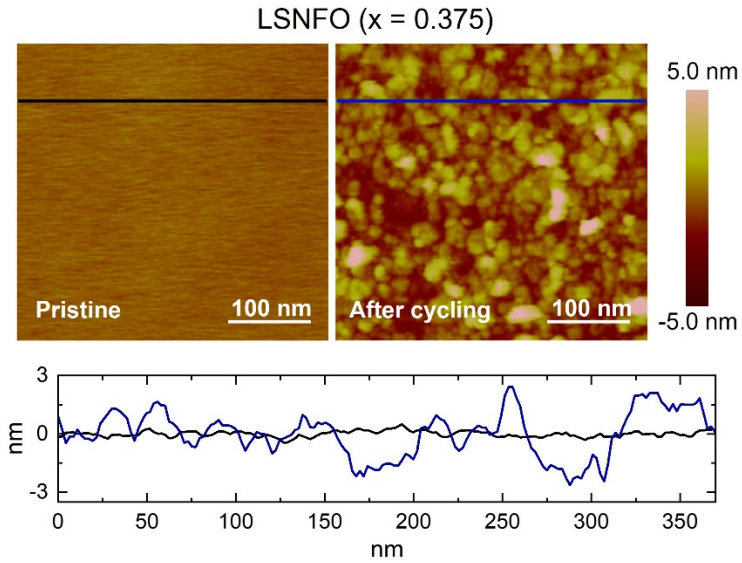

Fig. S6: Atomic force microscopy (AFM) images on selected LSNFO films show larger surface roughness after cycling.

Theoretical calculation for estimating surface Ni (Sample calculation for x = 0.375)

Assume idealized cubic cell structure for the perovskite oxide:

Unit cell area, $A_{u.c.} = c^2 = (3.822x10^{-10})^2 = 1.48x10^{-19}m^2$

where, c = Lattice parameter (in Å)

Geometric area of the electrode, $A_{geo} = \frac{\pi}{4}d^2 = \frac{\pi}{4}(\frac{1}{8}x0.0254)^2 = 7.9173x10^{-6}m^2$

Number of unit cells, $n_{u.c.} = \frac{A_{geo}}{A_{u.c.}} = 5.42x10^{13}$

With one B-site atom per perovskite unit cell,

Total Ni atoms, $N_{Ni} = n_{u.c.}x(1-0.375) = 5.42x10^{13}x(1-0.375) = 3.39x10^{13}atoms$

Estimated Ni atoms per m², $\frac{N_{Ni}}{A_{geo}} = \frac{3.39x10^{13}}{7.9173x10^{-6}} = 4.28x10^{18}\frac{atoms}{m^2}$

Estimated Ni atoms per nm², $\frac{4.28x10^{18}atoms}{(10^9)^2 \quad nm^2} 4.28\frac{atoms}{nm^2}$

Reference

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