

Fig. S1 24 surface structures of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.25}\text{Fe}_{0.75}\text{O}_3$ (110) surface. V denotes an oxygen vacancy. The Arabic numerals after Co refer to the layer of Co atom locating in the ABO_3 schematic structure. For example, Co1 refers to Co atom in the 1st ABO layer. When Co-atom is located in a specific ABO layer, there are six arrangements of two La and two Sr atoms in 4 sites. The roman numerals denote the specific structure of LSCF when Co in a determined layer.

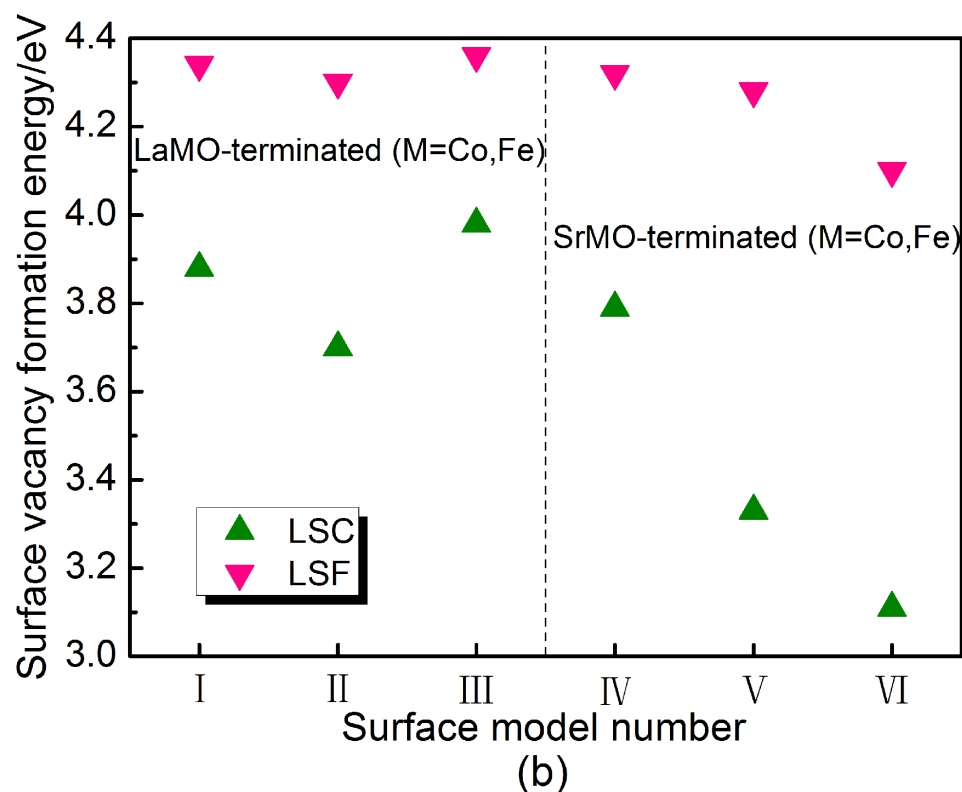
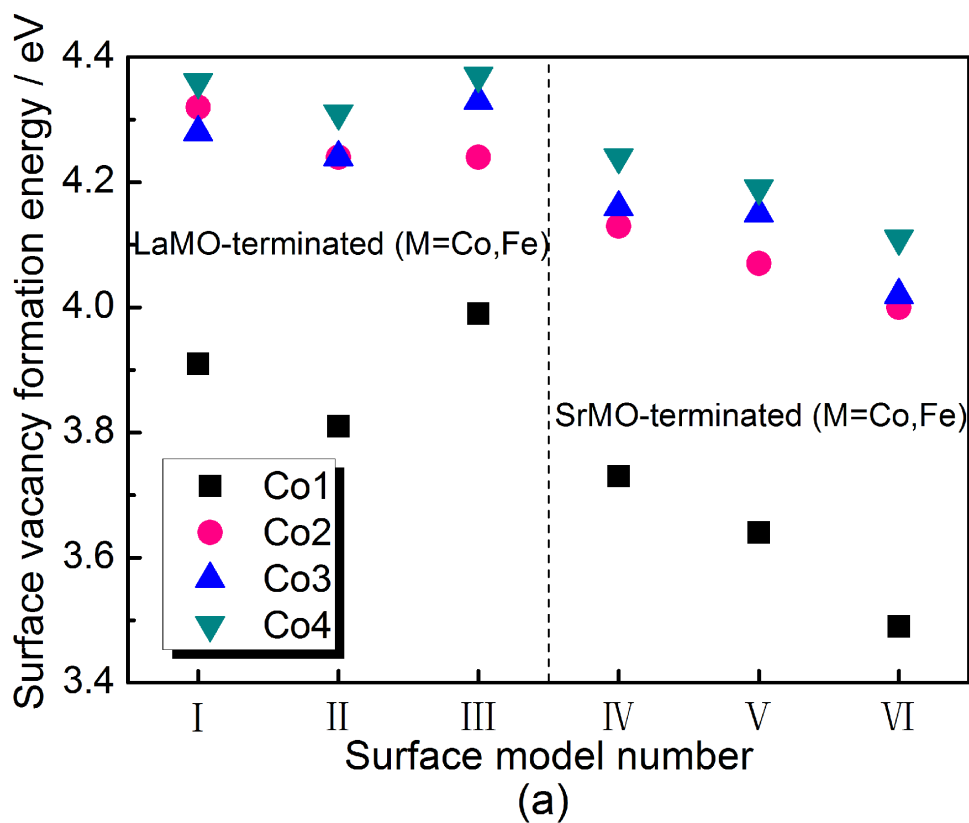


Fig. S2. Surface oxygen vacancy formation energies of (a) $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.25}\text{Fe}_{0.75}\text{O}_{2.875}$, (b) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.875}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{2.875}$ with various (110) surface models. Here, the surface model number in (a) is consistent with the notations for every surface model shown in Figure S1. Co1, Co2, Co3 and Co4 represent that Co taking the various layers in LSCF (110) surface, as shown in Fig. S1.

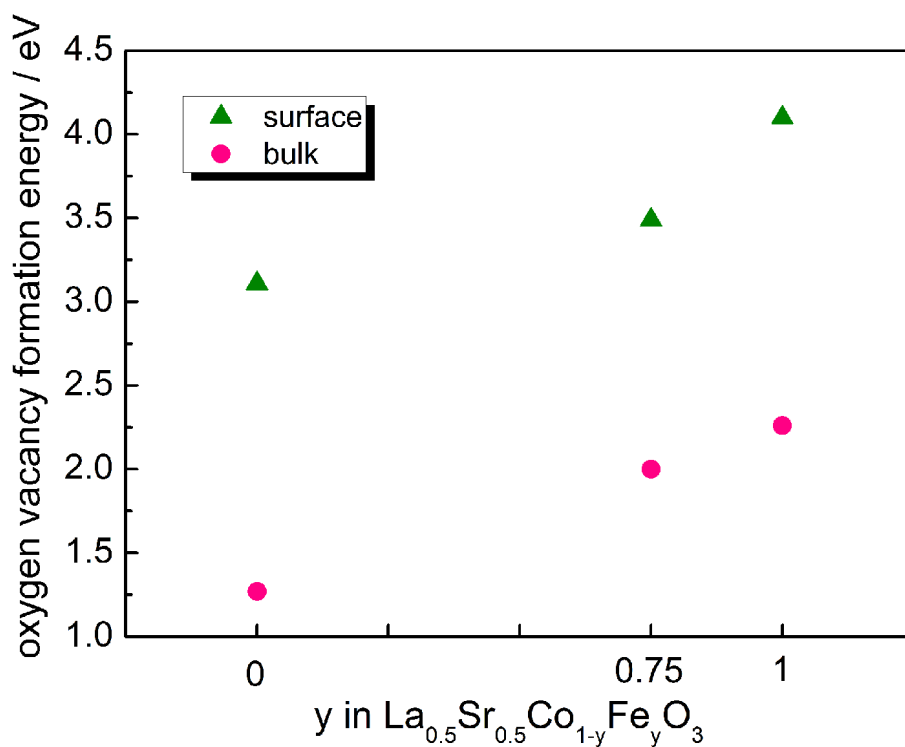


Fig. S3. Bulk and surface oxygen vacancy formation energy of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ ($y = 0, 0.75, 1$) cathode.

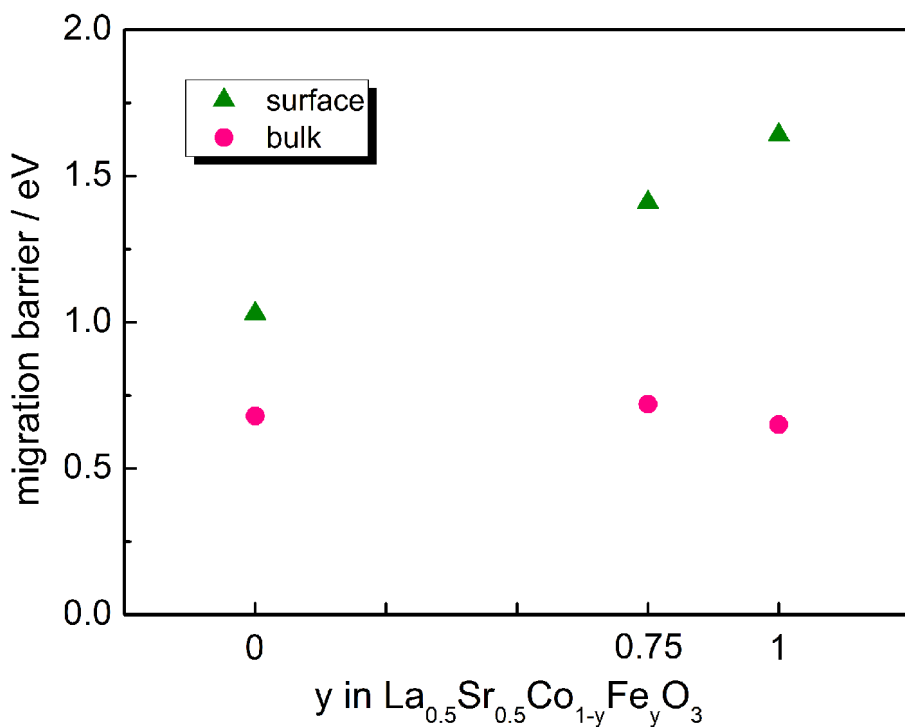


Fig. S4. Bulk and surface migration barriers for oxygen vacancy in $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ ($y = 0, 0.75, 1$) cathode.