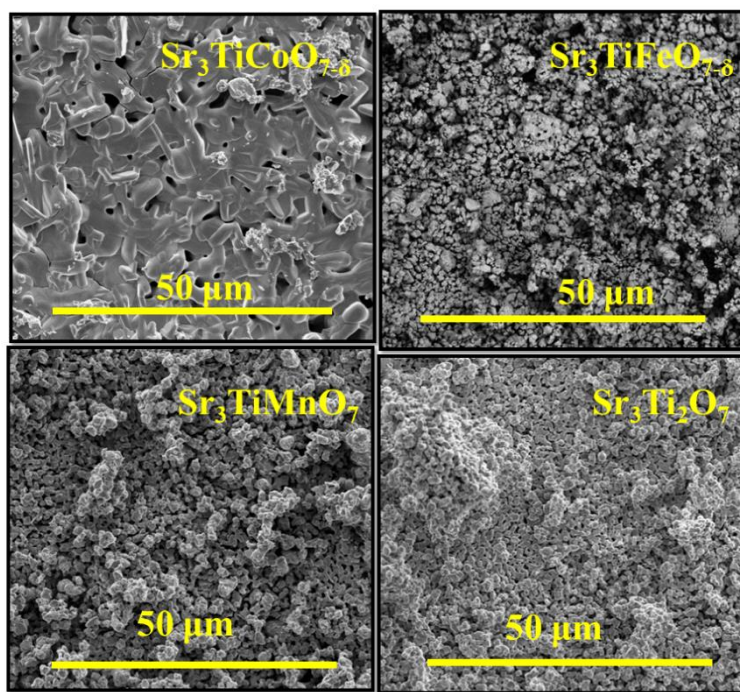
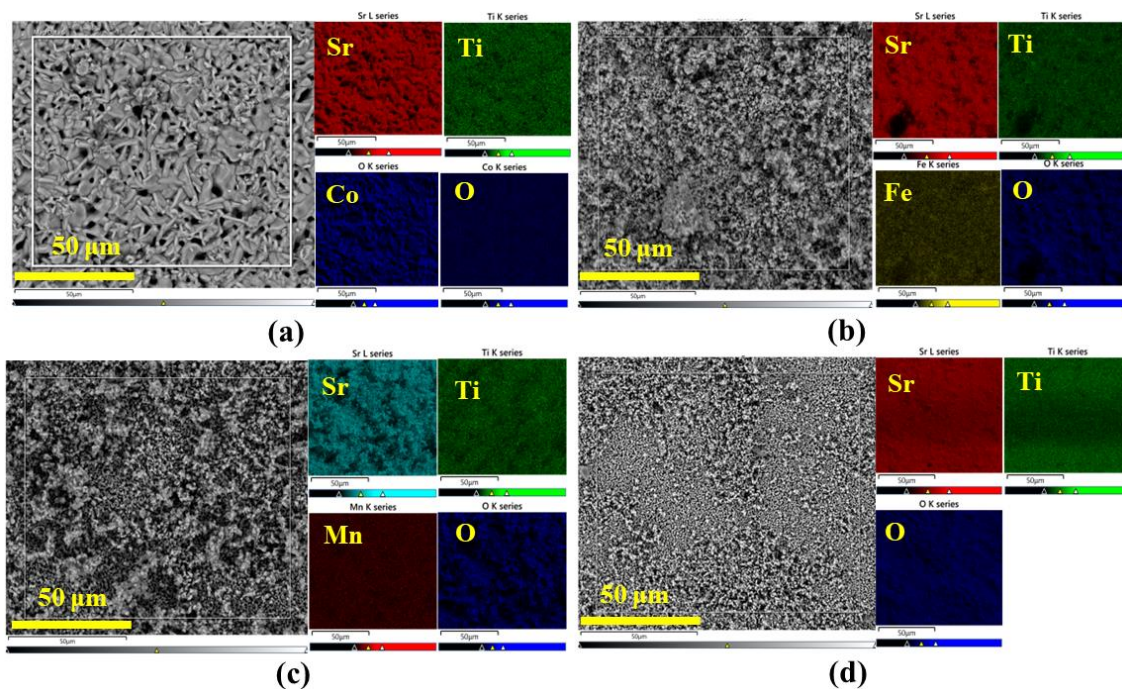


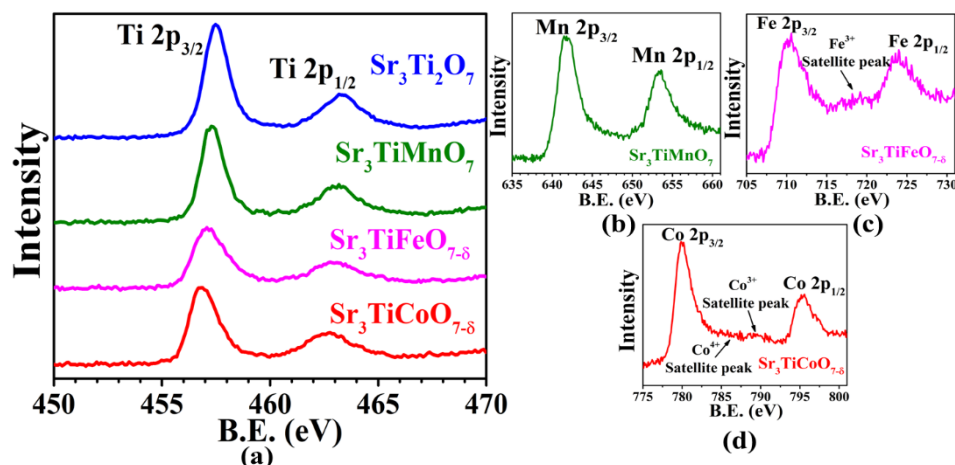
## Supporting Information



**Figure S1.** Scanning electron microscopy images.



**Figure S2.** EDX mapping analyses of (a)  $\text{Sr}_3\text{TiCoO}_{7-\delta}$ , (b)  $\text{Sr}_3\text{TiFeO}_{7-\delta}$ , (c)  $\text{Sr}_3\text{TiMnO}_7$ , and (d)  $\text{Sr}_3\text{Ti}_2\text{O}_7$ .



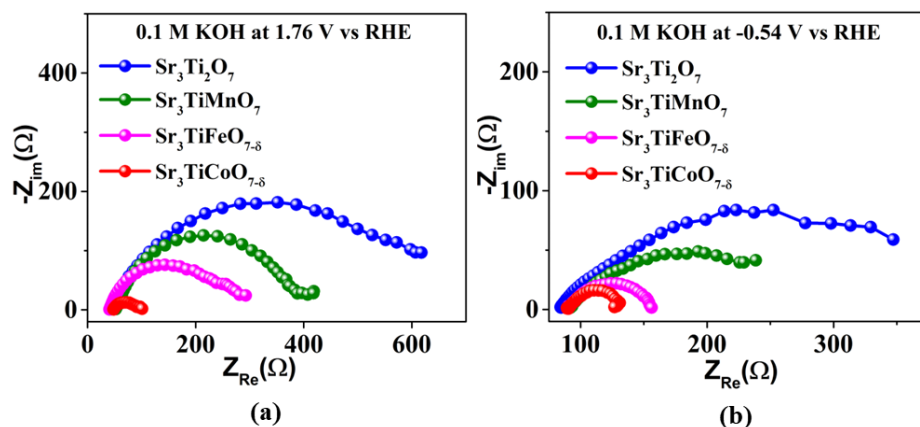
**Figure S3.** X-ray photoelectron spectroscopy data showing the Ti spectra for all compounds (a), Mn for  $\text{Sr}_3\text{TiMnO}_7$  (b), Fe for  $\text{Sr}_3\text{TiFeO}_{7-\delta}$  (c), and Co for  $\text{Sr}_3\text{TiCoO}_{7-\delta}$  (d).

In these XPS data, the Ti spectra of  $\text{Sr}_3\text{Ti}_2\text{O}_7$  and  $\text{Sr}_3\text{TiMnO}_7$ , which do not have oxygen-deficiency, show similar binding energies for the Ti  $2p_{3/2}$  peak. [55] While for  $\text{Sr}_3\text{TiFeO}_{7-\delta}$  and  $\text{Sr}_3\text{TiCoO}_{7-\delta}$ , which have oxygen-deficiency, the Ti  $2p_{3/2}$  peak is shifted to a slightly lower binding energy, indicating the reduction of some  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . [55, 56]

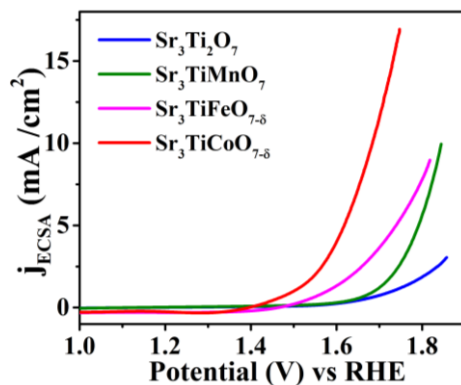
In the Mn spectrum for  $\text{Sr}_3\text{TiMnO}_7$ , the position of the  $2p_{3/2}$  peak,  $\sim 643$  eV, is consistent with tetravalent manganese. [57]

In the Fe spectrum for  $\text{Sr}_3\text{TiFeO}_{7-\delta}$ , the broad  $2p_{3/2}$  peak appears at  $\sim 710.6$  eV, [1, 58] with a shoulder at  $\sim 712$ - $713$  eV, [58] indicating the presence of both  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  ions, respectively. The satellite peak at  $\sim 8$  eV higher than the  $2p_{3/2}$  peak confirms the existence of  $\text{Fe}^{3+}$ . This is consistent with the presence of oxygen-vacancies.

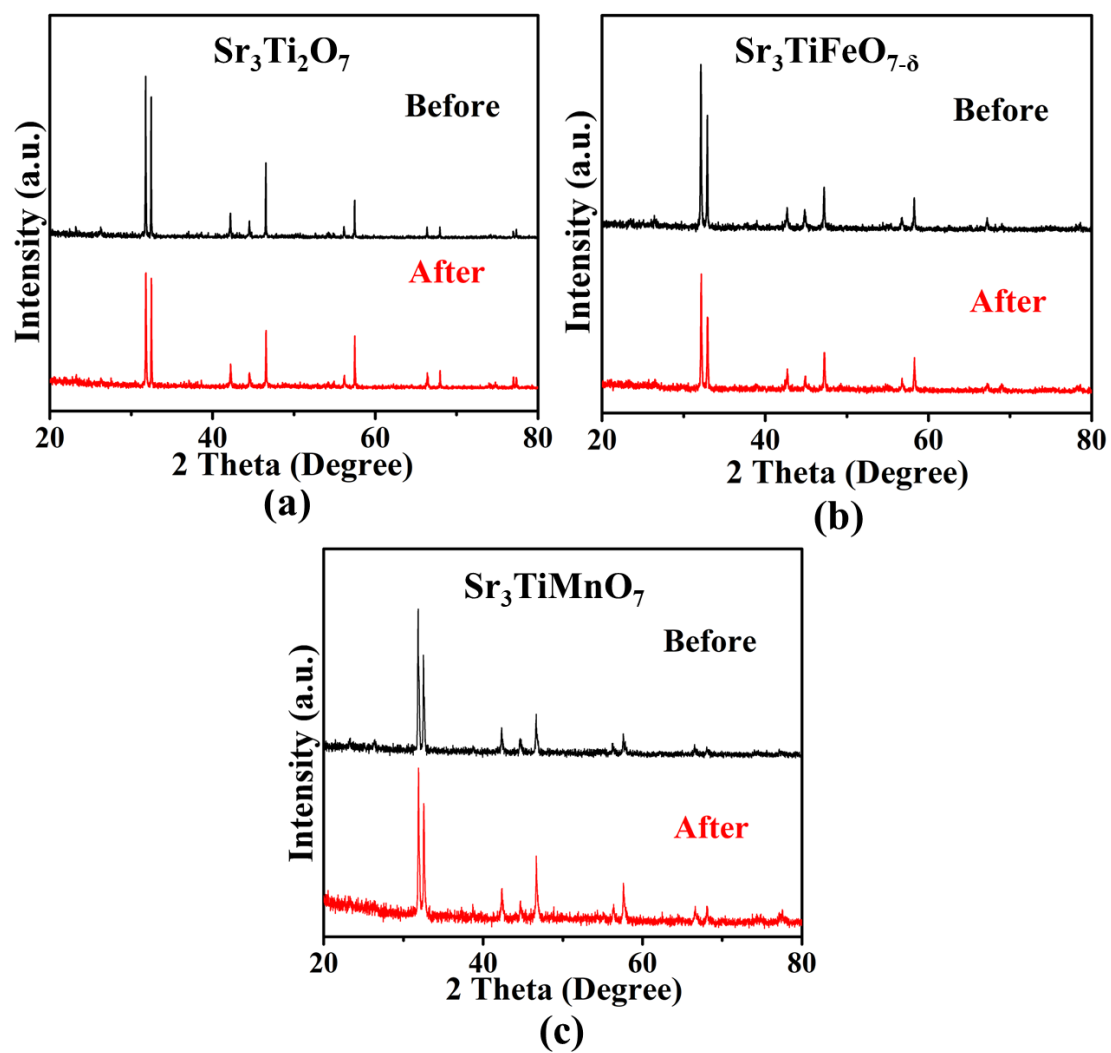
In the Co spectrum for  $\text{Sr}_3\text{TiCoO}_{7-\delta}$ , the  $2p_{3/2}$  peak above  $\sim 780$  eV with a shoulder on the high binding energy side indicates the co-existence of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$ . [59, 60] This is also consistent with the presence of two broad satellite peaks, one centered around  $\sim 786$  eV, indicative of  $\text{Co}^{4+}$ , [59, 60] and another centered around  $\sim 790$  eV, indicative of  $\text{Co}^{3+}$ . [60] This is consistent with the presence of oxygen-vacancies.



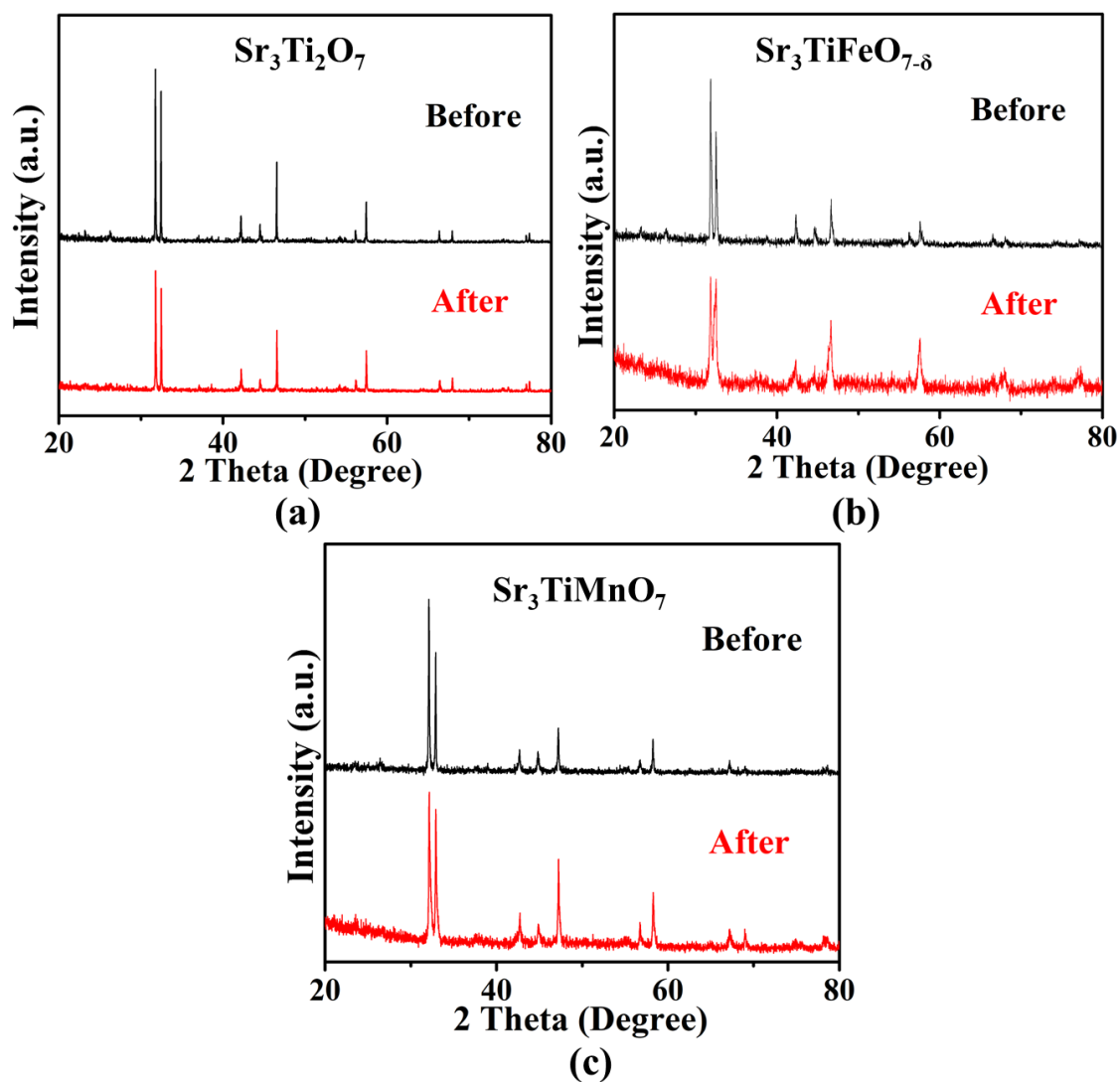
**Figure S4.** Impedance spectroscopy data to evaluate charge transfer resistance under (a) OER conditions, and (b) HER conditions. These data indicate that the trend in resistance is consistent with the trend in electrocatalytic activity, where the most active material has the smallest resistance.



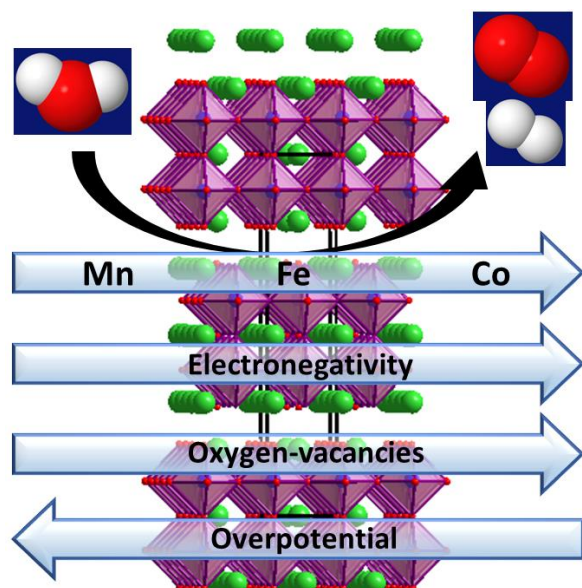
**Figure S5.** Polarization curves for OER in 0.1 M KOH with  $C_{dl}$  normalized current densities. [61]



**Figure S6.** X-ray diffraction data for (a)  $\text{Sr}_3\text{Ti}_2\text{O}_7$ , (b)  $\text{Sr}_3\text{TiFeO}_{7-\delta}$ , and (c)  $\text{Sr}_3\text{TiMnO}_7$ , before and after 100 cycles of OER in the 0.1 M KOH.



**Figure S7.** X-ray diffraction data for (a)  $\text{Sr}_3\text{Ti}_2\text{O}_7$ , (b)  $\text{Sr}_3\text{TiFeO}_{7-\delta}$ , and (c)  $\text{Sr}_3\text{TiMnO}_7$ , before and after 100 cycles of HER in the 0.1 M KOH.



**Figure S8.** The electronegativity increases from Mn to Fe and Co. The concentration of oxygen-vacancies increases from  $\text{Sr}_3\text{TiMnO}_7$  to  $\text{Sr}_3\text{TiFeO}_{7-\delta}$  and  $\text{Sr}_3\text{TiCoO}_{7-\delta}$ . The overpotential decreases from  $\text{Sr}_3\text{TiMnO}_7$  to  $\text{Sr}_3\text{TiFeO}_{7-\delta}$  and  $\text{Sr}_3\text{TiCoO}_{7-\delta}$ .

**Table S1.** OER and HER overpotentials at 10 mA cm<sup>-2</sup> ( $\eta_{10}$ ) for some Sr-based oxides.

	$\eta_{10}$ for OER	$\eta_{10}$ for HER	Electrolyte	Reference
Sr <sub>3</sub> TiCoO <sub>7</sub>	456 mV	-424 mV	0.1 M KOH	This work
Sr <sub>3</sub> TiFeO <sub>7</sub>	-	-452 mV	0.1 M KOH	This work
Sr <sub>3</sub> TiMnO <sub>7</sub>	-	-	0.1 M KOH	This work
Sr <sub>3</sub> Ti <sub>2</sub> O <sub>7</sub>	-	-	0.1 M KOH	This work
Sr <sub>2</sub> Fe <sub>1.5</sub> Mo <sub>0.5</sub> O <sub>6-<math>\delta</math></sub> (SFM)	~550 mV	~-440 mV	OER: 0.1 M KOH HER: 1 M KOH	[62]
SrTi <sub>0.1</sub> Fe <sub>0.85</sub> Ni <sub>0.05</sub> O <sub>3-d</sub> (STFN)	-	-	0.1 M KOH	[63]
Sr <sub>2</sub> FeMnO <sub>6-<math>\delta</math></sub>	~420 mV	~-480 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[29]
Sr <sub>2</sub> LaFeMnO <sub>7</sub>	-	-693 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[7]
Sr <sub>2</sub> LaCoMnO <sub>7</sub>	538 mV	-612 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[7]
SrLaCoO <sub>4-<math>\delta</math></sub>	510 mV	-542 mV	OER: 0.1 M KOH HER: 1 M KOH	[4]
SrLaCo <sub>0.5</sub> Fe <sub>0.5</sub> O <sub>4</sub>	520 mV	-622 mV	OER: 0.1 M KOH HER: 1 M KOH	[4]
SrLaFeO <sub>4</sub>	-	-691 mV	OER: 0.1 M KOH HER: 1 M KOH	[4]
Sr <sub>2</sub> FeCoO <sub>6-<math>\delta</math></sub>	280 mV	-490 mV	1 M KOH	[64]
SrCaFeCoO <sub>6-<math>\delta</math></sub>	270 mV	-390 mV	1 M KOH	[64]
SrNb <sub>0.1</sub> Co <sub>0.7</sub> Fe <sub>0.2</sub> O <sub>3-<math>\delta</math></sub>	500 mV	-361 mV	0.1 M KOH	[65]
Sr <sub>2</sub> LaMn <sub>2</sub> O <sub>7</sub>	-	-589 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[66]
Sr <sub>2</sub> LaFe <sub>3</sub> O <sub>8</sub>	~ 620 mV	~-800 mV	1 M KOH	[31]
SrLaAl <sub>1/2</sub> Mn <sub>1/2</sub> O <sub>4</sub>	-	-453 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[67]
SrLaAl <sub>1/2</sub> Fe <sub>1/2</sub> O <sub>4</sub>	-	-437 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[67]
SrLaAl <sub>1/2</sub> Co <sub>1/2</sub> O <sub>4</sub>	460 mV	-406 mV	OER: 0.1 M KOH HER: 0.5 M H <sub>2</sub> SO <sub>4</sub>	[67]



### Tafel equation

A simple electrochemical redox reaction can be described by the Butler-Volmer equation: [68, 69]

$$j = j_0 \left[ -e^{-\frac{\alpha n F \eta}{RT}} + e^{\frac{(1-\alpha) n F \eta}{RT}} \right]$$

Here,  $j$ ,  $j_0$ ,  $\alpha$ ,  $n$ ,  $\eta$ ,  $F$ ,  $R$ , and  $T$  indicate the total current (forward + backward), exchange current density, transfer coefficient, number of electrons transferred during the oxidation/reduction of a single molecule, overpotential, Faraday's constant, the universal gas constant, and the absolute temperature, respectively. In an oxidation reaction, when  $\eta \gg 0$ , the first exponential term of the above equation becomes 0 and, in the reduction reaction, when  $\eta \ll 0$ , the second exponential term of the above equation becomes 0. [68] Under those conditions, the Tafel equation, derived from the Butler-Volmer equation, can be described as:

$$\eta = a + b \log j \quad (\text{For an oxidation reaction})$$

$$\eta = a - b \log j \quad (\text{For a reduction reaction})$$

In the Tafel equation, the intercept,  $a$ , and slope,  $b$ , are:  $a = \frac{2.303RT}{\alpha n F} \log(j_0)$  and  $b = \frac{2.303RT}{\alpha n F}$

Obtaining the slope,  $b$ , of the Tafel plot will give the transfer coefficient,  $\alpha$ , which is the portion of the interfacial potential that promotes the reaction, whereas the remaining portion favors the opposite reaction. [68] Clearly, a smaller Tafel slope leads to a larger transfer coefficient, consistent with a more facile progress of the reaction:  $\alpha = 20303RT/bnF$