

# Spray Pyrolytically Synthesized Naturally Abundant Transition Metal Oxides and their Mixed Oxides for Efficient Electrochemical Splitting of Water to Hydrogen and Oxygen

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## Abstract:

In this study non-noble and non-rare metal-based naturally abundant first row transition metal oxides and their mixed oxides were synthesized by spray pyrolysis and used as electrocatalysts for the efficient splitting of water to hydrogen and Oxygen in an alkaline medium. The anodes of mixed oxides of nickel and cobalt (Ni-Co-oxide) having specific compositions (3:1 ratio) generated the much smaller Tafel slopes (210 mV decade<sup>-1</sup>) compared to 330 mV decade<sup>-1</sup> and 440 mV decade<sup>-1</sup> for Co-Oxide and Ni-oxide respectively indicating its enhanced electro-catalytic activity for oxygen evolution reaction (OER) during water splitting. Also, the anodes of mixed oxides of Ni and Fe (Ni-Fe-oxide) having specific compositions (4:1 ratio) generated the smaller Tafel slopes (360 mV decade<sup>-1</sup>) compared to 440 mV decade<sup>-1</sup> and 500 mV decade<sup>-1</sup> for Ni-oxide and Fe-oxide respectively for OER. At the measured potential of 1.0 V/SCE the current density of 130.0 mA cm<sup>-2</sup> was observed for water splitting at Ni-Co mixed oxide compared to 60.0 mA cm<sup>-2</sup>, 31.0 mA cm<sup>-2</sup>, 30.0 mA cm<sup>-2</sup> and 28.0 mA cm<sup>-2</sup> at mixed Ni-Fe oxide (4:1 ratio), Co-oxide, Ni-Oxide and Fe-oxide respectively. These results show more than four-fold increase in rate of water splitting at the mixed Ni-Co oxide and more than two-fold at mixed Ni-Fe oxide due to synergetic effects compared to their individual oxides. An order of magnitude of higher values of current density for water splitting on these electrodes compared to recently reported results can be attributed also to high internal surface area due to porosity and higher thickness of the oxide films synthesized by spray pyrolysis. Notably, thicker oxides synthesized by spray pyrolysis showed the similar trends in Tafel slopes as those of earlier reported thinner films of similar compositions.

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## 1. Introduction

Earth's ultimate recoverable source of oil, estimated to be 3.0 trillion barrels or  $1.7 \times 10^{10}$  trillion joules of energy is delivered by the Sun only in 39 hours [1-3]. Hence, solar water splitting which converts solar energy to hydrogen fuel, offers an ultimate alternative renewable *clean* energy solution. At the dawn of 21<sup>st</sup> century it is essential to harness Sun's near infinite clean energy for the benefit of our environment, eco-system and most importantly for the humanity at large. Because of ever increasing use of fossil fuel worldwide that generates erotic climate change, which will be responsible for disease, rising waters, food shortages, violent storms, droughts, shortage of food and worldwide poverty that will create instability and mass migration. The question is that - are we willing to accept the devastating consequence of climate change linked to combustion of fossil fuel to meet our energy needs? If not, then it requires us to quickly solve the challenging problem of developing alternative sources of clean energy in the form of solar fuel hydrogen from water that can replace fossil fuels.

For the generation of hydrogen from water in a clean manner, it is ideal to develop sunlight-driven photoelectrochemical cell for direct photosplitting of water using suitable photoelectrodes. The stability of photoelectrodes for water splitting to hydrogen under sunlight illumination in a photoelectrochemical cell (PEC) is crucial for economically viable system that can last for years. Since the photoelectrodes will be continually immersed in the electrolyte solution and illuminated with direct solar radiation, a long life is a daunting challenge, which has not been achieved as of yet [4-18] during the long search for last 40 years. Also, no sign of achieving this in sight in near future. However, the world needs such a system without much delay. Hence, at this time, it will be advantageous to

develop highly efficient electrocatalytic electrodes for use in sunlight-driven water splitter powered by solar modules [19, 20] or wind power for large scale production of hydrogen. This will then be an effective way to store Sun's near infinite energy in the form of hydrogen fuel.

To produce hydrogen and oxygen from water it requires an external applied potential to overcome the thermodynamic, ohmic and kinetic barriers of the water-splitting reaction. Pollution free hydrogen fuel generation and the flexibility of choosing the external power sources such as solar cell modules [19] or wind have made water electrolysis the most desirable compared to traditional processes that use fossil fuels as hydrogen source. The abundant and cost effective solar energy captured using optimum design of silicon-based solar cell modules [20] can be used to generate the power required to drive the water electrolysis reaction. However, the present water electrolyzer's low current efficiency has made the process less competitive compared to steam reforming methanol or natural gas [21]. Most of the research efforts to improve the water electrolysis efficiency have been focusing on the energetically challenging water oxidation to generate oxygen at anodes and thereby facilitate hydrogen evolution reaction (HER) at cathodes during water splitting reaction. In alkaline medium, at cathodes the HER occurred as,

$$4\text{H}_2\text{O} (l) + 4e^- \rightarrow 2\text{H}_2 (g) + 4\text{OH}^- (aq) \quad (1)$$

at anodes the OER occurred as,

$$4\text{OH}^- (aq) \rightarrow \text{O}_2 (g) + 2\text{H}_2\text{O} (l) + 4e^- \quad (2)$$

The addition of reactions (2) and (3) gives the overall water splitting reaction asreaction as,

$$2\text{H}_2\text{O} (l) \rightarrow 2\text{H}_2 (g) + \text{O}_2 (g) \quad (3)$$

Earlier work [22] included noble metals and rare metal oxides such as RuO<sub>2</sub> or IrO<sub>2</sub> for oxygen evolution reaction (OER). However, the dependence on rare metals is not ideal because a massive worldwide manufacturing of

noble/rare metal-based water-splitter will drive up their price and reduce their availability further. Perhaps the most suitable approach is to use naturally abundant transition metals and their oxides or a combination of transition metals and their oxides to minimize the overpotential required for oxygen evolution reaction at the anode surface. Ni, Co and their oxides have been extensively studied individually or as alloys as electrocatalytic electrodes for the oxygen evolution reaction [22-32].

Previous investigations on transition metals M-single oxides (M= Ni, Co or Fe) targeted on enhancing the catalytic activity for OER by modifying the surface morphologies and studying their behavior during OER. However, the extent to which the catalytic activity of these transition metal single oxides toward OER can be enhanced was found to be rather limited. The other available alternative to use naturally abundant transition metal based electrodes for OER is the first row transition metal mixed oxides. The synergetic effects of the later on electrocatalytic activities for OER were recognized earlier [33-40]. The effect of methods of synthesis of these mixed oxides electrodes and their composition on electro-catalytic activity for OER were also noted [30]. In previous studies the thick layers of mixed oxides were mainly synthesized by hot pressing transition metal oxide powders [41, 42], very thin films by electrodeposition [37-40] and as well as by spin coating [35, 36]. The use of thin films helped to identify the compositions for optimum electrocatalytic effect for water splitting reaction by identifying lowest Tafel slopes at low current densities in avoiding the effect of surface thickness and porosity.

Also, for the large-scale hydrogen evolution reaction (HER) during water splitting it was attempted to replace noble metal by high surface area naturally abundant metal foams such as nickel foam [43] or its compound such as nickel phosphides of various compositions and morphologies in acidic electrolyte [44]. However, for hydrogen evolution reaction (HER) in alkaline medium, Ni-Mo, and Ni-Mo-Cd were used and patented [45 - 47].

In this study we focused on synthesizing relatively thick films of mixed Ni-Co-oxides, mixed Ni-Fe oxides with different atomic ratios, individual Ni-oxide, Co-oxide and Fe-oxides by spray pyrolysis method on conducting fluorine doped tin oxide (FTO) coated glass substrate for large scale generation of hydrogen. The electrocatalytic activities of the mixed Ni-Co-oxide and Ni-Fe oxide and their individual oxides used as anodes for oxygen evolution in basic medium were assessed in terms of Tafel slopes and current density and compared with those of individual oxides. The surface morphologies of these oxide films and composition of these oxide electrodes were characterized using the scanning electron microscopy (SEM) and the presence of relevant elements were identified by the respective energy dispersive x-ray spectroscopic (EDS) spectra.

## 2. Experimental

### 2.1. Synthesis of Nickel, Cobalt and Iron Oxide and their Mixed Oxides

Commercially available fluorine doped tin oxide (FTO) coated conducting glass substrates were cleaned in a sonicator using acetone, Acetone: Di-water (50:50) and Di-water respectively. Each step lasted 30 minutes. The cleaned FTO glass substrates were then dried under dry Argon gas. The resistivity of the resulting ITOs was found to be within 14-20 ohm cm at room temperature. Aqueous solutions of 0.05 M Ni-Chloride, 0.05 M Co-nitrate and 0.05 M Fe-Nitrate were used as spray solutions to synthesize Ni-oxide, Co-oxide and Fe-oxide respectively.

Different volume ratios of these aqueous solutions were also used to synthesize mixed Ni-Co oxides and mixed Ni-Fe oxides. The spray operation was carried out for a total of 30 sec having three 10 sec spray periods on a FTO conducting glass substrate at a temperature of 180°C using a pneumatic nozzle and oxygen as the carrier gas with a pressure of 20 psi. In between each spray period there were intervals of ~ 10 min for the substrate temperature to be raised back to 180°C on the hot plate. A conducting silver epoxy was applied to the four edges of the FTO glass to ensure a uniform electrical conductivity across the electrode surface area during water electrolysis. After the spray the silver epoxy at the edges of the electrodes was covered with a non-conductive resin based epoxy.

### 2.2. Electrochemical Measurements

Linear sweep voltammetry was used as the main tool to assess the electrocatalytic performance of these electrodes toward OER. A three-electrode configuration in a single-compartment cell was used, with Ni-Co mixed oxides, Ni-Fe mixed oxide, Ni-oxide, Co-oxide or Fe-oxide as a working electrode (anode), platinum wire as a counter electrode (cathode), and SCE as a reference electrode. The single compartment cell was filled with 2.5 M KOH as an electrolyte solution. The linear sweep CV curves of the catalysts were obtained using a scanning potentiostat (Versa STAT 3 running Versa Studio software, Princeton Applied Research). A scan rate of 50 mV s<sup>-1</sup> was used to minimize the extra resistances developed at the electrode-solution interfaces by the bubbles of oxygen and hydrogen gases generated during water splitting reactions.

### 2.3. SEM and EDS Measurements

Scanning electron microscopy (SEM) was used to characterize the surface morphology of the spray pyrolytically synthesized thin films using a high-resolution Hitachi S-3400 SEM having a 2.0 kV focus voltage. The Hitachi S-3400 SEM equipped with a Bruker Quantax energy dispersive spectrometer was also used for energy-dispersive x-ray spectroscopic (EDS) analysis. Samples were mounted on a double-sided carbon tape affixed to an Aluminum specimen holder. The EDS spectra were collected at a working distance of 10 mm and an accelerating voltage of 15 KV.

## 3. Results and Discussion

Figure 1 shows the current density versus the external applied potential curves for mixed Ni-Co oxide, Ni-oxide, Co-oxide, Fe-oxide and bare FTO during OER. In this Figure the mixed Ni-Co oxide anode (synthesized using 3:1 volume ratio of 0.05 M NiCl<sub>2</sub> and 0.05 M Co(NO<sub>3</sub>)<sub>2</sub> in spray solution and sprayed for total of 30 sec) showed the highest and bare FTO showed the lowest electrocatalytic activity toward OER during water splitting. The observed sharp rise in current density for OER at Ni-Co-mixed oxides at 0.7 V/SCE compared to those at the individual Ni and Co oxides indicates that the presence of Co along with Ni generates active mixed oxide surfaces having lower overpotential for OER. For example, at 1.0 V/SCE the observed current density of 130.0 mA cm<sup>-2</sup> at mixed Ni-Co-oxide is over 4-fold higher compared to observed current density of ~ 30.0 mA cm<sup>-2</sup> on their individual oxides. Similarly, at 1.0 V/SCE the observed current density of 60.00 mA cm<sup>-2</sup> at mixed Ni-Fe oxide (synthesized using 4:1 volume ratio of 0.05 M NiCl<sub>2</sub> and 0.05 M Fe(NO<sub>3</sub>)<sub>3</sub> in spray solution and sprayed for total of 30 sec) is over 2-fold higher compared to observe current density of 28.00 mA cm<sup>-2</sup> on Fe-oxide itself as it is observed in Figure 1 and Figure 2. It should be noted that the current density for the OER did not enhance further when the film thicknesses were attempted to increase by increasing the spray pyrolysis time beyond 30 sec. This observation indicates that a too thick film loses its electronic conductivity by producing less compact layers.

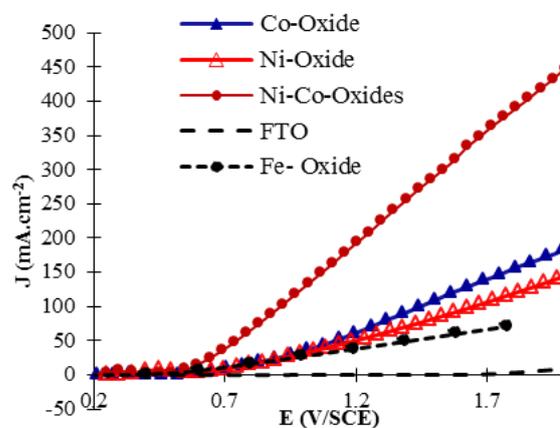


Figure 1: Current density, J (mA cm<sup>-2</sup>) versus applied potential (E, V/SCE) during OER at bare FTO conducting glass, Ni-oxide, Co-oxide, Fe-oxide and mixed Ni-Co-oxide electrodes

The observed broad peaks prior to oxygen evolution in Figure 3 indicates the existence of direct relationship between the position of these peaks and an early oxygen evolution at lower onset potential. In the case of mixed Ni-

Co-oxide electrodes of 3:1 ratio shows the formation of electro-chromic Ni-oxide at lower potential compared to other compositions [22]. Consequently, mixed Ni-Co oxide of 3:1 ratios shows the highest synergetic electrocatalytic effect towards OER. However, in Figure 2 no clear broad peaks are observed for mixed Ni-Fe oxides of various compositions. In this case the mixed oxide having Ni:Fe ratio of 4:1 shows highest electrocatalytic effect towards OER during water splitting. However, the synergetic effect between nickel and iron oxides towards electrocatalysis of OER was found lower than that of nickel and cobalt oxides. But cost wise iron will be lower in cost than cobalt to offset its lower synergetic electrocatalytic effect compared to cobalt. It is important to note that the best electrocatalytic activity we obtained for the film synthesized by spray pyrolysis having Ni:Fe ratio of 4:1 ratio was found consistent with the best result obtained for the same ratio in a previous study [35] in which very thin films were synthesized by spin coating followed by UV-light exposure and heating at 100 °C for an hour. Electrochemically synthesized thinner films Ni-Fe oxide of Ni:Fe of 9:1 generated the best electrocatalytic activity though it was lower than their Ni-oxide/Ni-oxyhydroxide sample [38]. However, in the present study the thicker films of Ni-Fe oxide having 9:1 ratio synthesized by spray pyrolytic method did not show better electrocatalytic effect compared to 4:1 ratio (see Figure 2). But our finding of best electrocatalytic activity of 3:1 ratio of Ni:Co in mixed Ni-Co oxide was found consistent with what was reported earlier [36, 38].

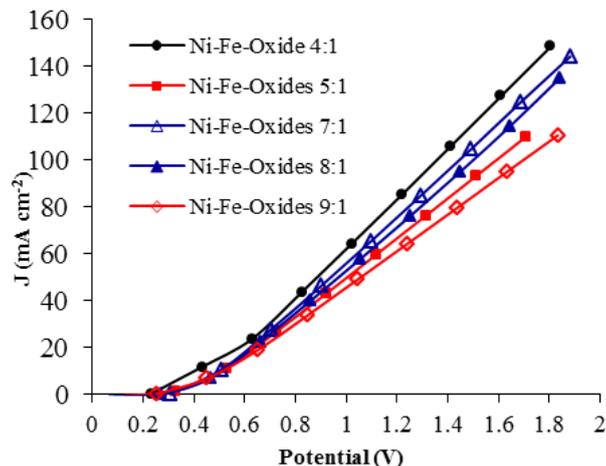


Figure 2: Current density,  $J$  ( $\text{mA cm}^{-2}$ ) versus applied potential (V/SCE) during OER at mixed Ni-Fe oxides of various compositions all deposited on FTO coated glass substrate. The currents for OER were measured in 2.5 M KOH solution at a scan rate of  $50 \text{ mV s}^{-1}$

Figure 4 shows the Tafel plots of these five metal oxides. The mixed Ni-Co oxide anode sprayed pyrolytically on FTO exhibits the lowest Tafel slope of  $210 \text{ mV/decade}$  compared to  $330 \text{ mV/decade}$  for Co-oxide and  $440 \text{ mV decade}^{-1}$  for Ni-oxide anodes for OER. A Tafel slope of  $360 \text{ mV decade}^{-1}$  for mixed Ni-Fe oxide and  $500 \text{ mV decade}^{-1}$  for Fe-oxide anodes for OER were observed during water splitting. The lowest Tafel slope for mixed Ni-Co oxide and mixed Ni-Fe oxide compared to their individual oxides

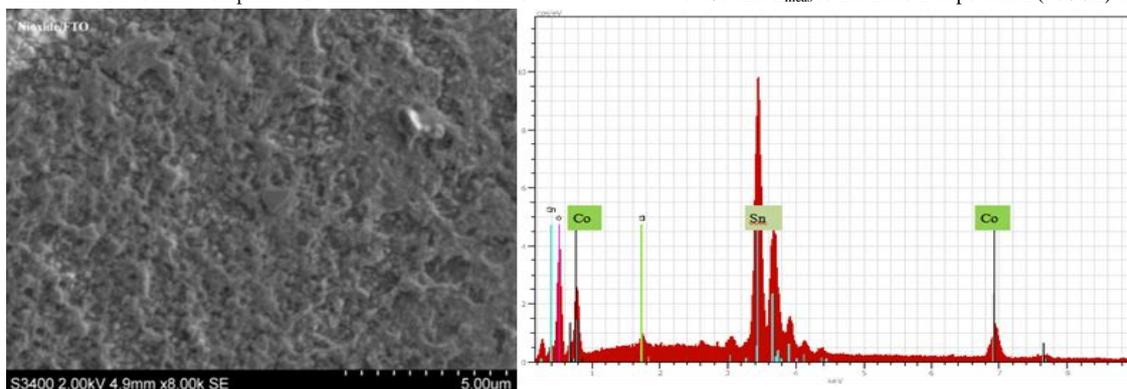


Figure 5: SEM pictures and EDS results of Co-oxide on FTO coated glass substrate

distinctly indicates their higher electrocatalytic activity due to synergetic effect [32, 33] of mixed oxides that generated active surface sites for efficient OER. These Tafel slopes are much higher in values compared to those reported earlier on very thin films but notably have the similar trends. The higher values of Tafel slopes indicate resistive thicker and porous film produced by spray pyrolysis on resistive FTO substrate for the spray time of 30 sec as is observed in the SEM pictures (see Figure 5-Figure 9). Also, at such high current densities bubbles of oxygen and hydrogen gases, generated considerable resistances at the electrode- solution interfaces.

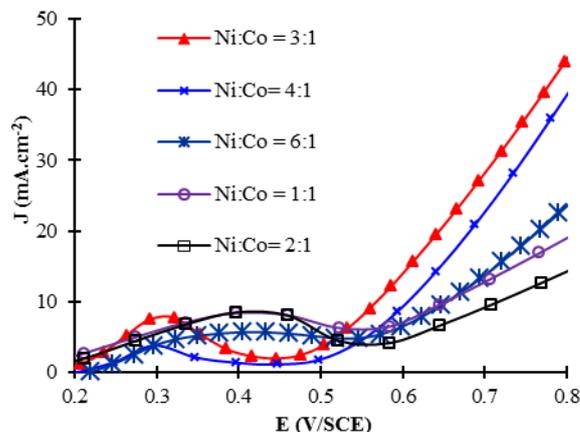


Figure 3: Current density,  $J$  ( $\text{mA cm}^{-2}$ ) versus applied potential (E, V/SCE) during OER at mixed Ni-Co-oxides of various compositions

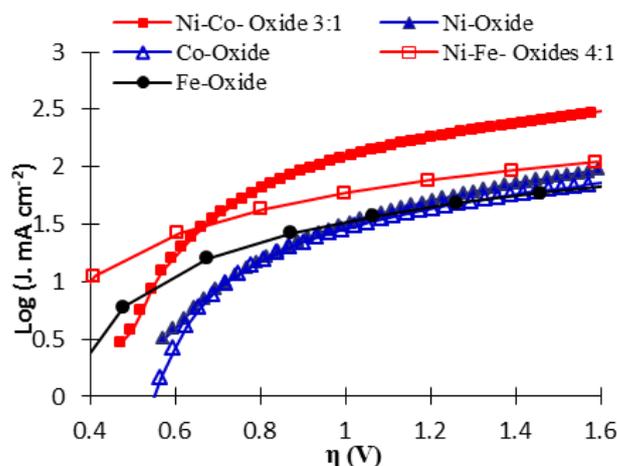


Figure 4: Tafel plots obtained from the Log (current density,  $J$ ) vs overpotential,  $\eta$ ) for OER at mixed Ni-Co oxide, mixed Ni-Fe oxide, Ni-oxide, Co-oxide and Fe-oxide electrodes. The overpotentials for OER were obtained using  $\eta = E_{\text{meas}} - E_{\text{OER}}^0$  where  $E_{\text{OER}}^0 = 0.116 \text{ V/SCE}$  is the standard oxygen evolution potential in 2.5 KOH electrolyte having measured pH of 14.81 and  $E_{\text{meas}}$  is the measured potential (V/SCE) during OER

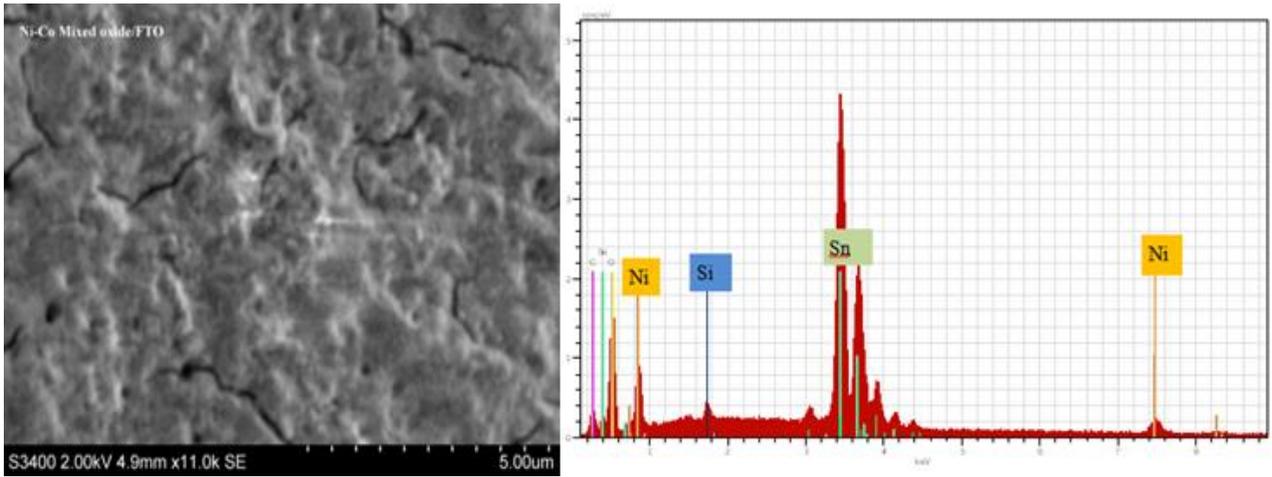


Figure 6: SEM pictures and EDS results of Ni-Oxide on FTO coated glass substrate

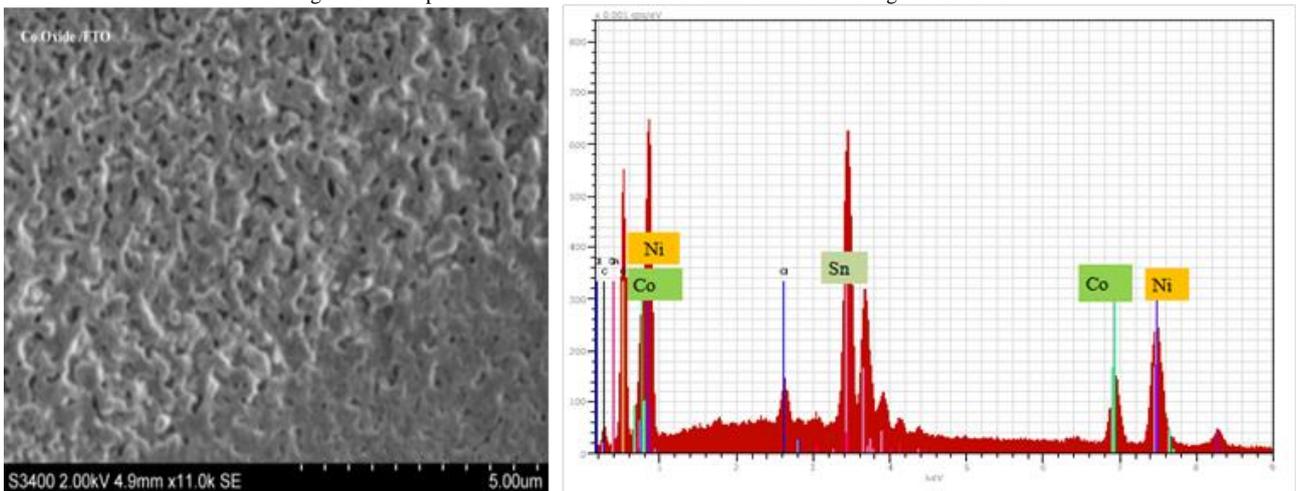


Figure 7: SEM pictures and EDS results of Mixed Ni-Co oxide (3:1 ratio) on FTO coated glass substrate

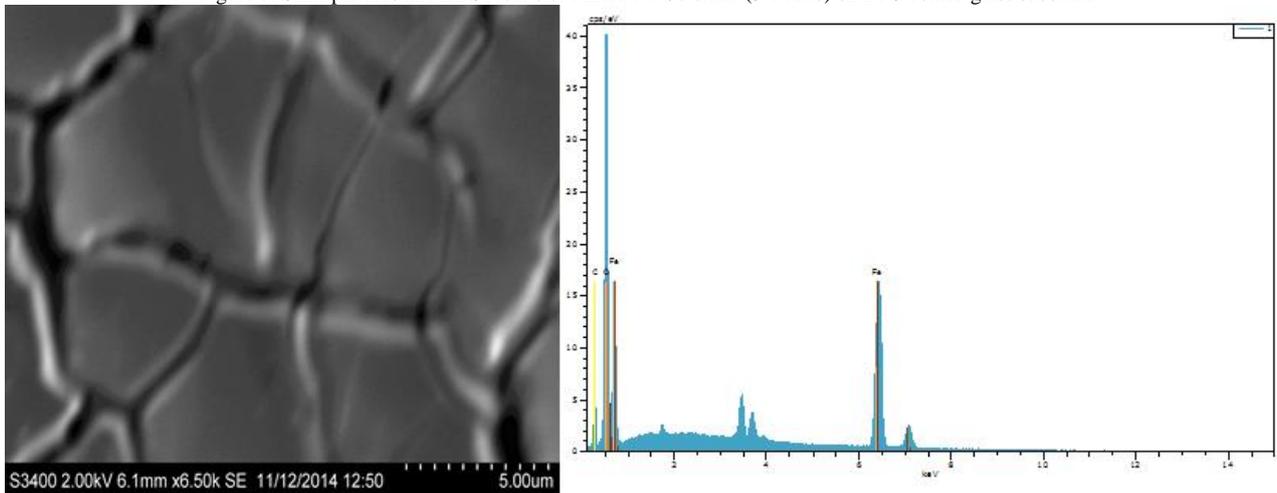


Figure 8: SEM pictures and EDS results of Fe-oxide on FTO coated glass substrate

The surface morphologies obtained from the scanning electron microscopy (SEM) pictures and the corresponding energy dispersive x-ray spectroscopic (EDS) spectra for Co-oxide, Ni-oxide and mixed Ni-Co-oxides (3: 1 ratio), Fe-oxide and mixed Ni-Fe-oxide (4:1 ratio) on FTO coated glass are shown in Figure 5 to 9 respectively. The microgram in Figure 5 indicates the rough and porous surface of Co-oxide and the corresponding EDS data shows the presence of Co, Sn and O on the surface as expected. Similarly, the microgram in Figure 6 shows a less rough surface of Ni oxide and the corresponding EDS data showed the presence of Ni, Sn and O. The microgram of mixed Ni-Co oxide (Figure 7) shows the roughest and most porous surface. The corresponding EDS data shows the

presence of Ni, Co, Sn and O as expected. The microgram of Fe-oxide (Figure 8) shows the smooth and cracked surface. The corresponding EDS data shows the presence of Fe, Sn and O as expected. However, the microgram of mixed Ni-Fe oxide as shown in Figure 9 exhibits rougher surface with some porosity. The corresponding EDS data shows the presence of Ni, Fe, Sn and O as expected. These rough and porous surfaces are responsible for the enhanced internal surface area that helped to generate an order of magnitude higher current densities higher values of Tafel slopes compared to recently reported results on very thin films [35-40]. The internal surface area for the rough and porous surface could be  $\sim 10^4$  times higher than the geometrical surface area [37].

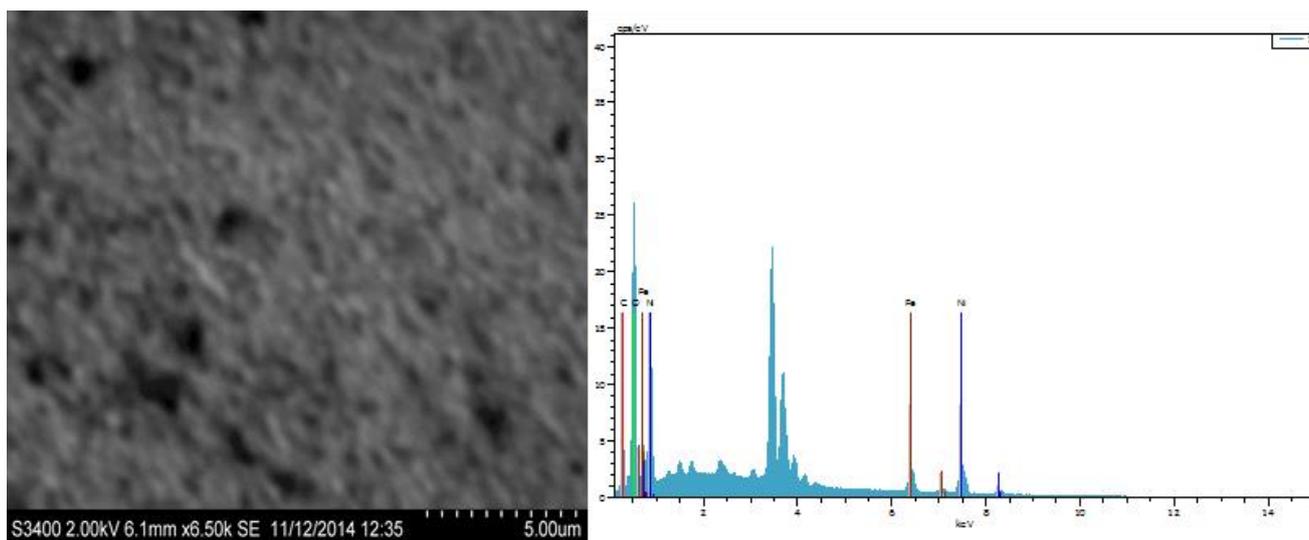


Figure 9: SEM pictures and EDS results of Mixed Ni-Fe-oxide (4:1 ratio) on FTO coated glass substrate

#### 4. Conclusions

Electrocatalytically active porous with high internal surface area Ni-oxide, Co-oxide, Fe-oxide, mixed Ni-Co-oxide and mixed Ni-Fe oxide anodes can be synthesized by spray pyrolysis method on fluorine doped tin oxide (FTO) coated glass substrate. The synergetic effect of mixed oxides helped to generate more active electrocatalytic porous high internal surface area anodes for highly efficient oxygen evolution reaction (OER) during water splitting reactions. Thus, these naturally abundant mixed transition metal oxide anodes can be coupled with active non-noble metal foams or mixed metal cathodes to develop solar cell and wind powered electrolyzers for large-scale generation of solar fuel hydrogen by efficient water splitting. Future studies should be focused on the synthesis of naturally abundant ternary transition metal oxides and perovskite oxides by spray pyrolytic method for efficient water oxidation for large-scale production of hydrogen. In future studies better conducting substrate other than FTO coated glass such as graphite or acid etched Ti-metal should be used for spray pyrolytic deposition of these oxides.

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