Hierarchical Urchin-like Spinel \( \text{Cu}_x\text{Co}_{3-x}\text{O}_4 \) Particles as Oxygen Evolution Reaction Catalysts in Alkaline Medium

R A E Acedera, and M D L Balela
Sustainable Electronic Materials Group, Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines, Diliman, Quezon City, Philippines 1101

E-mail: rose_anne.acedera@upd.edu.ph, mlbalela1@up.edu.ph

Abstract. In this work, spinel \( \text{Cu}_x\text{Co}_{3-x}\text{O}_4 \) (\( x = 0.00, 0.50, 1.00, 1.50 \)) was synthesized through a typical ethanol-assisted hydrothermal route. The effect of the incorporation of copper on the resulting morphology, structure, and oxygen evolution reaction (OER) activity of the spinel Co oxides was investigated. In general, Cu-doped samples exhibited improved OER activity associated to the reduction of electrical resistivity of the spinel due to the presence of \( \text{Cu}^{2+} \) into the lattice. Further, the ionic bonding of \( \text{OH}^- \) with \( \text{Cu}^{2+} \) is weaker relative to the \( \text{Co}^{3+} \) ions at the octahedral sites, which could have facilitated OER better. Among the Cu concentration experimented, \( \text{Cu}_{0.5}\text{Co}_{2.5}\text{O}_4 \) exhibited the best OER catalytic with an onset overpotential and Tafel slope of about 271 mV and 100.4 mV·dec\(^{-1}\), respectively. This is attributed to its better conductivity due to the absence of a resistive secondary CuO phase.

1. Introduction
Oxygen evolution reaction (OER) has been a central process in most energy storage and conversion systems today [1]. However, regardless of the nature of the medium used, it proceeds through a four-step electron transfer mechanism. Its complex nature results to slow reaction kinetics and high electrochemical overpotentials, thereby drastically lowering the efficiency of energy conversion [2, 3]. To resolve such drawbacks, catalysts are used in practice to facilitate OER. At present, catalysts based on precious metals such as Pt [4], Ir [5], and Ru [6] exhibited superior electrocatalytic activities. However, their high cost, scarcity, and limited stability in alkaline environment hinder their industrial application [7, 8].

Alternative OER electrocatalysts include those which are based on earth abundant transition metals, such as spinel oxides [9], perovskites [10], layered double hydroxides [11], chalcogenides [12], carbides [13], and sulfides [14]. Particularly, spinel transition metal oxides showed promising electrocatalytic activity due to their good electrical conductivities, and the presence of active sites for oxygen adsorption and release in their structures. These resulted from the efficient electron transfer between the metals of different valences in the spinel structure [15, 16]. Among these spinel transition metal oxides, cobalt (II, III) oxide (\( \text{Co}_3\text{O}_4 \)) is regarded as one of the best heterogeneous OER electrocatalysts with its excellent activity, and stability, even in alkaline electrolytes [17-20]. It is the most stable oxide of cobalt, consisting of \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) ions in the tetrahedral and octahedral sites, respectively.
To further improve its intrinsic OER activity, Co$_3$O$_4$ has been doped with different metals. For example, Co$_3$O$_4$ was doped with Li, which resulted in lower electrical resistivity and onset potential by about 50 mV [21]. On the other hand, Ni-doped Co$_3$O$_4$ showed better OER activity than the undoped oxide even at Ni-doping as low as 0.25 atomic % [22]. The increased activity was observed up to 0.50% Ni-doping (Co$_{2.985}$Ni$_{0.015}$O$_4$). However, it was reduced when the amount of Ni was further increased [22]. Moreover, a comparative study on the catalytic behavior of M$_x$Co$_{3-x}$O$_4$ (M = Li, Ni, Cu) showed that OER activity increased in the order Co$_3$O$_4$ < Ni$_x$Co$_{3-x}$O$_4$ << Cu$_x$Co$_{3-x}$O$_4$ < Li$_x$Co$_{3-x}$O$_4$, indicating that Cu is a viable dopant over other metals due to its cost-effectivity [23].

A number of studies has reported OER activity enhancement of Co$_3$O$_4$ through Cu-doping. However, most of these articles made use of Cu$_x$Co$_{3-x}$O$_4$ thin films or coatings [24-25]. Specifically, the use of hierarchically-structured Cu$_x$Co$_{3-x}$O$_4$ particles as OER electrocatalyst has not been reported elsewhere. In the present paper, hierarchical urchin-like, spinel Cu$_x$Co$_{3-x}$O$_4$ nanostructures were synthesized using ethanol-assisted hydrothermal route and tested for OER catalysis. The effects of copper incorporation on the morphology, structure and catalytic activity of Co$_3$O$_4$ were investigated.

2. Experimental details

2.1. Catalyst synthesis

The spinel Cu$_x$Co$_{3-x}$O$_4$ electrocatalysts were synthesized through a typical ethanol-assisted hydrothermal route as reported previously [26]. All of the chemical reagents were analytical grade and used without further purification. In a typical procedure, cobalt nitrate hexahydrate [Co(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich, 98%] and copper nitrate hemi pentahydrate [Cu(NO$_3$)$_2$·2.5H$_2$O, Sigma-Aldrich, 98%] were mixed accordingly to prepare four compositions of Cu$_x$Co$_{3-x}$O$_4$ (x = 0.00, 0.50, 1.00, and 1.50). The total amount of metal salts was held constant at 5.00 mmol. The metal salts were added into a solution of 1.00 g cetyltrimethylammonium bromide (CTAB, C$_{19}$H$_{42}$BrN, Loba Chemie, 99%) and 2.00 g urea (CH$_4$N$_2$O, Techno Pharmchem, 99.5%) in a 1:2 ethanol-water mixed solvent [10.00 mL anhydrous ethanol (C$_2$H$_5$OH, Ajax Finechem, 100%) and 20.00 mL distilled water]. To ensure homogeneous mixing, the solutions were stirred at 300 rpm for 1 h, and then transferred into 100 mL Teflon-lined steel autoclaves. These were held at 100 °C for 10 h. After the reaction, the precipitates were collected via centrifugation, washed three times with deionized H$_2$O and ethanol, and then dried at 100 °C for 2 h. Calcination was done at 400 °C for 6 h, at a heating rate of 1 °C·min$^{-1}$.

2.2. Material characterization and electrochemical studies

The resulting morphologies of the samples was examined in a field-emission scanning microscope (FESEM, Hitachi SU 8230). Crystal structure and phase identification were performed by X-ray diffraction (XRD, PanAlytical X’pert PRO MPD, Cu Kα).

Electrochemical measurements were done on a Biologic S-150 instrument using a three-electrode cell setup, with Cu$_x$Co$_{3-x}$O$_4$/ carbon fiber paper (CFP), Ag/AgCl (MetrOhm), and Pt wire as the working, reference, and counter electrodes, respectively. The working electrode was prepared by depositing the catalyst ink, made up of a dispersion of 80.00 mg active material, and 20.00 mg polytetrafluoroethylene (PTFE, (C$_2$F$_4$)$_n$, Sigma-Aldrich) binder in minute amount of anhydrous ethanol, onto previously cleaned 1.50 x 1.00 cm$^2$ CFP. The mass loading of the active material was ~ 0.50 mg cm$^{-2}$.

All electrochemical experiments were done at room temperature, ambient pressure, and in 1.00 M KOH electrolyte (pH = 13.81). OER polarization curves were obtained through linear sweep voltammetry (LSV) from 0.10 to 1.10 V (vs. Ag/AgCl electrode) at a scan rate of 1.00 mV·s$^{-1}$. On the other hand, the stability of the working electrode was assessed by subjecting it to 500 cycles of polarization from 0.40 to 0.70 V (vs. Ag/AgCl) at a rate of 100 mV·s$^{-1}$. To further ascertain the stability of the electrodes, chronoamperometry (CA) and chronopotentiometry (CP) were done by applying 0.60 V (vs. Ag/AgCl), and 1.00 mA·cm$^{-2}$ current density onto the working electrode for 2 h.
All obtained potential values were converted against the reversible hydrogen electrode (RHE) using the equation \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \cdot \text{pH} + E^\circ_{\text{Ag/AgCl}} \) where \( E_{\text{RHE}} \) is the converted potential with respect to RHE, \( E_{\text{Ag/AgCl}} \) is the experimental potential value obtained, and \( E^\circ_{\text{Ag/AgCl}} \) is the standard reduction potential of the Ag/AgCl (3.30 M KCl) electrode at 25 °C. Subsequently, the overpotential values were then calculated with respect to the thermodynamic potential equal to 1.23 V (vs. RHE).

3. Results and Discussion

3.1. Material characterization

Figure 1a shows the XRD patterns of the synthesized \( \text{Cu}_{x}\text{Co}_{3-x}\text{O}_4 \) powders. For the undoped sample (\( x = 0.00 \)), the peaks identified at 2\( \theta \) = 18.99, 31.33, 36.86, 38.72, 44.89, 55.67, 59.34, 65.26, and 77.4° can be well-indexed to the (111), (220), (311), (222), (400), (422), (511), (440), and (531) planes of spinel \( \text{Co}_3\text{O}_4 \) (JCPDS 43-1003) [27]. On the other hand, the diffraction pattern of \( \text{Cu}_{0.5}\text{Co}_{2.5}\text{O}_4 \) (\( x = 0.50 \)) is identical to that of the parental spinel \( \text{Co}_3\text{O}_4 \), showing no additional peaks associated to secondary phases. This indicates that all Cu\(^{2+} \) ions have been incorporated entirely into the oxide, and their substitution with Co\(^{2+} \) did not alter the spinel structure [22]. However, as the amount of Cu was increased (\( x = 1.00 \), and 1.50), additional peaks at 2\( \theta \) = 35.58, 48.71, and 61.5° appeared. These peaks were attributed to the (002), (202), and (113) planes of monoclinic CuO, which formed as a secondary phase [28]. In fact, the amount of CuO apparently increased as \( x \) was changed from 1.00 to 1.50. As seen in Figure 1b, the peak at around 38.50°, which are due to both (222) spinel oxide and (111) CuO peaks increased in intensity. These are in agreement with previous reports that pure Cu-Co oxide can be obtained at \( x \) values less than 1.00 [25].

![Figure 1](image_url)

Figure 1. (a) XRD patterns of \( \text{Cu}_{x}\text{Co}_{3-x}\text{O}_4 \) and, (b) magnified view of the plot from 2\( \theta \) = 30° to 47.5°

Table 1 lists down the structural parameters calculated for the oxides. For all samples, peak broadening was observed, indicative of their small crystallite size. The crystallite size was calculated using the Debye-Scherrer approximation from the broadening of the (311) peak. On the other hand, it is clear from Figure 1b that peak positions shifted to lower 2\( \theta \) values as Cu was incorporated. These small displacements imply enlargement of the crystal lattice, reflected by the increasing lattice parameter values in Table 1. This could be ascribed to the larger radii of Cu\(^{2+} \) (0.73, 0.57 Å) in contrast to that of Co\(^{2+} \) and Co\(^{3+} \) (0.52, 0.58 Å) in the octahedral, and tetrahedral sites of the spinel [22, 29-30]. On the other hand, the calculated lattice parameter of the undoped and Cu-doped sample is comparable with the reported values for spinel \( \text{Co}_3\text{O}_4 \) (8.08 Å) [31], and of \( \text{Cu}_{0.92}\text{Co}_{2.08}\text{O}_4 \) (8.10 Å), respectively [25].
Table 1. Structural parameters of Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub>

| Sample | 2θ [°] | d spacing [Å] | Lattice Parameter, a [nm] | FWHM [°] | Crystallite size [nm] |
|--------|--------|---------------|--------------------------|----------|----------------------|
| x = 0.00 | 36.860 | 2.436 | 8.078 | 0.380 | 22.036 |
| x = 0.50 | 36.720 | 2.445 | 8.108 | 0.520 | 16.097 |
| x = 1.00 | 36.760 | 2.442 | 8.099 | 0.580 | 14.433 |
| x = 1.50 | 36.740 | 2.444 | 8.104 | 0.560 | 14.948 |

Figure 2 shows the FESEM images of the synthesized Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> oxides. The undoped Co<sub>3</sub>O<sub>4</sub> are spherical with a mean diameter of 63.507 nm (SD = 14.626) as seen in Figure 2a-b. The particles, however, agglomerated to reduce to their high surface energy due to their small particle size. Upon Cu-incorporation, a significant change in morphology was observed. Urchin-like microparticles, composed of nanowires of increasing mean diameter of 13.351 (SD = 66.664), 26.662 (SD = 32.273), and 31.482 nm (SD = 20.643), were produced for x = 0.50, 1.00, and 1.50, respectively. The formation of urchin-like particles can be explained by the anisotropic growth promoted by the incorporation of the dopant Cu<sup>2+</sup> ions. Anisotropic growth results from the difference in the adsorption energies of the dopant on the different facets of the host spinel Co<sub>3</sub>O<sub>4</sub> [32].

The formation of nanosheets can also be observed at x = 1.00 and became more evident at x = 1.50. These nanosheets could be the secondary CuO phase detected by XRD at excess Cu. The CuO nanosheets were possibly formed from Cu(OH)<sub>2</sub>, which were generated from the hydrolysis of Cu<sup>2+</sup> ions in a strong alkaline solution. Calcination at 400 °C dehydrates Cu(OH)<sub>2</sub>, thereby producing CuO. Release of water results to the formation of O-Cu-O bridges between Cu(OH)<sub>2</sub> layers. This leads to oriented attachment of the particles, thereby forming a sheet-like structure [33-34].

Figure 2. Low and high magnification FESEM images of Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> with (a, b) x = 0.00, (c, d) x = 0.50, (e, f) x = 1.00, and (g, h) x = 1.50

3.2. Electrochemical properties of the synthesized Co<sub>3</sub>O<sub>4</sub> and Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> powders

Figure 3a shows the LSV polarization curves from 1.10 to 2.20 V (vs. RHE) of the Co<sub>3</sub>O<sub>4</sub> and Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub>/CFP electrode in 1.00 M KOH. Undoped Co<sub>3</sub>O<sub>4</sub> exhibited the largest onset potential for OER of 1.637 V and a corresponding overpotential of 407 mV. Upon Cu-doping, at x = 0.50, higher OER activity was achieved as the onset potential and the overpotential decreased to 1.501 V, and 271 mV, respectively. This can be attributed to the decrease of the electrical resistivity of the oxide, and the stronger bond of Co<sup>3+</sup> to OH<sup>-</sup> over Cu<sup>2+</sup> [35]. M-OH bond strength was found to be a critical parameter
for OER activity as it determines the ease of breaking up the bond between the metal and the OH\(^{-}\) ions adsorbed at the beginning of the reaction. A stronger M-OH bond needs higher energy to dissolve the bond, leading to larger overpotential. On the other hand, as the amount of Cu was further increased, the onset potential shifted more positively to 1.531 (x = 1.00) and 1.542 V (x =1.50). Although the catalytic activity improved compared to the undoped Co\(_3\)O\(_4\), the enhancement was offset due to the presence of a resistive CuO phase in the samples [36].

The abrupt increase in the measured current densities after the onset indicated the beginning of OER. The required potential to reach a 10 mA/cm\(^2\)-current density, a metric significant in solar fuel production, were found to be 1.520, 1.643, 1.680, and 1.696 V at x = 0.00, 0.50, 1.00, and 1.50, respectively. Correspondingly, Tafel measurements were determined from the LSV polarization data. As shown in Figure 3b, the slope of the undoped sample was 102.1 mV·dec\(^{-1}\), and those of the doped oxides were 100.4 (x = 0.50), 103.2 (x = 1.00), and 107.4 mV·dec\(^{-1}\) (x = 1.50). These values further prove the high activity of Cu\(_{0.5}\)Co\(_{2.5}\)O\(_4\) over Co\(_3\)O\(_4\). The sustained linear behavior even at high current density regions imply fast electron transfer and mass transport across the electrode-electrolyte interface [37].

![Image](image.png)

**Figure 3.** Electrochemical characterization of the CuxCo3-xO4/CFP electrode with (a) LSV polarization curves from 1.10 to 2.20 V vs. RHE, and corresponding (b) Tafel plots.

Figure 4a shows the cyclic voltammograms of the samples from 1.20 to 1.55 V (vs. RHE). All the electrodes exhibited characteristic redox peaks, which could be attributed to the Co\(^{3+}/Co^{4+}\) redox couple [24):

\[
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{Co-O}_2 + e^- + \text{H}_2\text{O}
\]  

(1)

As the applied potential increases, energy becomes sufficient such that the bond between Co\(^{4+}\) ions and the adsorbed O\(_2\) is severed. This bond breaking then results to the release of O\(_2\) gas [38]. A less positive anodic peak value, therefore, indicates better OER catalytic property because it implies earlier OER onset. Herein, the anodic peak potential values at x = 0.00, 0.50, 1.00, and 1.50 are 1.506, 1.463, 1.467, and 1.470 V (vs. RHE), respectively. These values correspond to the Co\(^{3+}/Co^{4+}\) redox couple peak positions for Cu\(_x\)Co\(_{3-x}\)O\(_4\) electrodes (1.43 to 1.53 V vs RHE) [24, 39-40]. Similarly, Cu\(_{0.5}\)Co\(_{2.5}\)O\(_4\) exhibited the smallest anodic peak potential, which agrees with the results of the LSV. Moreover, the onset potential for all electrodes shifted in correspondence to the variation of the position of the Co\(^{3+}/Co^{4+}\) redox peak [24].
Figure 4. (a) Cyclic voltammograms from 1.20 to 1.55 V vs. RHE, (b) LSV plots after 500 cycles of polarization, and corresponding (c) Tafel plots, and (d) CA plot of the Cu0.5Co2.5O4 electrode (inset: CP plot)

To determine the stability of the OER electrodes, 500 cycles of polarization in the potential window 1.40 to 1.80 V were done. Figure 4b-c show the LSV curves and the corresponding Tafel plots of the samples before and after the stability test. The onset potentials increased by 2.70 to 2.56% at x = 0.00 to 1.50. Correspondingly, the Tafel slopes were also larger by 2.45 to 2.10%. These prove that the Cu_xCo_{3-x}O_4/CFP electrodes remained stable even after numerous cycles of polarization. Furthermore, it can be seen in Figure 4d that the measured chronoamperometric (~ 6 mA·cm^{-2}), and chronopotentiometric response (1.55 V) of Cu_{0.5}Co_{2.5}O_4/CFP remained constant even after 2 h, establishing further the stability of the best performing electrode.

4. Conclusion
In conclusion, spinel Cu_xCo_{3-x}O_4 (x = 0.00, 0.50, 1.00, and 1.50) powders were synthesized through ethanol-assisted hydrothermal route. Incorporating Cu^{2+} ions onto the spinel Co_3O_4 lattice resulted to a drastic change in morphology from agglomerated, spherical particles to micro urchins composed of nanowires. Furthermore, doping beyond x = 0.50 yielded a secondary CuO phase. For the OER catalytic activity testing, Cu^{2+} doping caused improvements to the performance of Co_3O_4. Cu_{0.5}Co_{2.5}O_4 was found to be the best performing electrode with onset overpotential and Tafel slope as low as 1.501 V, and 100.4 mV·dec^{-1}, respectively. Increasing Cu content beyond x = 0.50 resulted to lower OER activity due to the presence of a resistive CuO phase. Stability tests proved the durability of the Cu_xCo_{3-x}O_4/CFP electrodes, with the observed minimal change in their onset potentials, and Tafel slopes after 500 polarization cycles from 1.4 to 1.8 V.

Acknowledgment
This study is supported by the Commission on Higher Education (CHED)-Newton Agham Institutional Links, under the project “Affordable Electrolyzer Technology based on Transition Metal
“Catalyst for Energy Storage” and Robert Cheng – Uratex 2019 College of Engineering Professorial Chair. Funding for conference attendance was also provided by UP College of Engineering.

References
[1] Doyle S R L and Lyons M E G The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design 2010 (Switzerland)
[2] Hu A T, Wang Y, Zhang L and Tang T 2019 Applied Catal. B, Environ. 243 175–182
[3] Li R, Zhou D, Luo J, Xu W, Li J, Li S and Cheng 2017 J. Power Sources 341 250–256
[4] Sung M and Kim J 2018 Int. J. Hydrogen Energy 43 2130-2138
[5] Papaderakis A, Tsiplakides D, Balomenou S and Sotiropoulos S 2015 J. Electroanal. Chem. 757 216–224
[6] Ma Z, Zhang Y, Liu S, Xu W, Wu L, Hsieh Y C, Liu P, Zhu Y, Sasaki K, Renner J N, Ayers K E, Adzic R R and Wang J X 2018 J. Electroanal. Chem. 819 296–305
[7] Guo Y, Guo D, Ye F, Wang K and Shi Z 2017 Int. J. Hydrogen Energy 42 17038–17048
[8] Si C, Zhang Y, Zhang C, Gao H, Ma W, Lv L and Zhang Z 2017 Electrochim. Acta. 245 829–838
[9] Bocca C 1999 Int. J. Hydrogen Energy 24 699–707
[10] Han B, Grimaud A, Giordano L, Hong W T, Diaz-Morales O, Lee Y, Hwang J, Charles N, Stoerzinger K A, Yang W, Koper M T M and Shao-horn Y 2018 J. Phys. Chem. C 122 8445-8454
[11] Xie T, Min J, Liu J, Chen J, Fu D, Zhang R, Zhu K and Lei M 2018 J. Alloys Compd. 754 72–77
[12] Zhang T, Zhu Y and Lee J Y 2018 J. Mater. Chem. A
[13] Wygant B R, Kawashima K and Mullins C B 2018 ACS Energy Lett.
[14] Peng L, Shah S and Wei Z 2018 Chinese J. Catal. 39 1575-1593
[15] Zeng K and Zhang D 2010 Prog. Energy Combust. Sci. 36 307–326
[16] Zhang Y, Zhang C, Gao H, Ma W, Lv L and Zhang Z 2017 Electrochim. Acta. 245 829–838
[17] Yang X, Li H, Lu A Y, Min S, Idriss Z, Hedhili M N, Huang K W, Idriss H and Li L J 2016 Nano Energy 25 42–50
[18] Asadizadeh S, Amirnasr M, Meghdadi S, Fadaei Tirani F and Schenk K 2018 Int. J. Hydrogen Energy 10 4922-4931
[19] Ye K H, Zhou S A, Zhu X C, Xu C W and Shen P K 2013 Electrochim. Acta 90 108–111
[20] Balela M D L, Angostura T J E, Domingo A M F and Facal C G P 2018 Key Eng. Mater. 775 336–341
[21] Wu X and Scott K 2013 Int. J. Hydrogen Energy 8 1–7
[22] Singhal A, Bish A and Irusta S 2018 J. Electroanal. Chem. 823 482–491
[23] Nikolov I, Darkaou R, Zhecheva E, Stoyanova R, Dimitrov N and Vitanov T 1997 J Electroanal Chem
[24] Wu X and Scott K 2011 J. Mater. Chem. 21 12344-12351
[25] Chi B, Lin H and Li J 2008 Int. J. Hydrogen Energy 33 4763–4768
[26] Wen W, Wu J M and Tu J P 2012 J. Alloys Compd. 513 592–596
[27] Zhang Y, Zhou X, Zhang F, Tian T, Ding Y and Gao H 2017 J. Catal. 352 246–255
[28] Barkaoui S, Dhaouadi H, Kouass S and Touati F 2015 Int. J. Light Electron Opt. 126 1047–1051
[29] Franken T and Palkovits R 2015 Appl. Catal. B Environ. 176 298–305
[30] Xu Q, Su Y, Wu H, Cheng H, Guo Y, Li N and Liu Z 2014 Curr. Nanosci. 11 107–112
[31] Ibupoto Z H, Khun K, Beni V, Liu X and Willander M 2013 SNL 7926–7938
[32] Han X, Wahl S, Russo P and Pinna N 2018 Nanomaterials 8 249
[33] Cudennec Y, Lecerf A 2003 Solid State Sci 5 1471–1474
[34] Shahmiri M, Ibrahima N A, Zainuddin N, Azim N, Bakhtyar B, Zaharim A and Sopian K 2013 WSEAS Transactions on Environment and Development 243–252
[35] Wu J, Huang X, Berglund K, Lu X, Xiaohua, Feng X, Larsson R and Shi Y 2018 CSTE 162 86-92
[36] De Koninck M, Poirier S and Marsan B 2006 J. Electrochem. Soc. A2103-2110
[37] Park Y S, Park C S, Kim C H, Do Kim Y, Parkand S and Lee J H 2016 J. Korean Phys. Soc. 69 1187–1190
[38] Pittkowski R, Krtil P and Rossmeisl J 2018 Curr. Opin. Electrochem. 12 218 – 224
[39] Fradette N and Marsan B 1998 J. Electrochem. Soc. 145 2320– 2327
[40] La Rosa-Toro A, Berenguer R, Quijada C, Montilla F, Morallón E and Vázquez J L 2006 J. Phys. Chem. B 110 24021–24029.