Synthesis and Electrocatalytic Activity Evaluation of Nanoflower Shaped Ni-Pd on Alcohol Oxidation Reaction

Mohammad Shamsuddin Ahmed and Seungwon Jeon*

Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea

We are reporting a synthesis of nickel and palladium (Ni-Pd) nanoflowers with excellent size and Calendula-like shapes using a wet-chemistry method for efficient alcohol oxidation reaction (AOR). The nanoflower structure has shown to have electrocatalytic activity to monohydric short carbon chain containing alcohols (C1-C4; methanol, ethanol, propanol and n-butanol). The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) reveal that the Ni-Pd nanoflowers catalyst has different electronic behavior due to flower-like structure and comparatively higher degree of alloy formation. The transmission electron microscopy (TEM) images showed a Calendula flower-like shape and crystalline structure of Ni-Pd. The electrochemical properties of the catalyst have been evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) in 1 M KOH electrolyte. For the first time, a comparative kinetic analysis has been investigated between four alcohol’s catalysis. The higher electrocatalytic activity has increased in the order of C3 > C4 > C1 > C2. The overall AOR kinetic study has determined that the Ni-Pd is favorable to Ni mediated alloyed formation and flower-like structure.

The addition of transition metal like nickel (Ni) to Pd can obviously improve the overall electrocatalytic activities of Pd because of the bimetallic promotional effect. Also the size and surface morphology of electrocatalysts are crucial for their catalytic activities. Moreover, the d-band shifts to the center and the changes of segregation energy of added metals also responsible for higher catalytic activity of bimetallic Pd alloyed catalysts have been proved density functional theory. With view in mind, the tailored design and synthesis of Pd with Ni has attracted much attention because of their low-cost and superior catalytic activities. Therefore, the Ni-Pd nanoflowers as new catalysts will attract much interest because of the special conjunction effects of alloyed formation and nanoflower-like structure. Up to now, however, it still remains a great challenge to find a method to fabricate the Ni-Pd nanoflowers.

Based on the above discussion, we have synthesized the Calendula flower like Ni-Pd nanoflowers via a simple chemical process, which has the following merits: (a) the Ni-Pd nanoflowers are easily synthesized by a simple wet-chemical process; (b) the Ni as second metal element can be easily hybridized with Pd into Ni-Pd nanoflowers; and (c) the Pd in Ni-Pd nanoflowers can be electrochemically utilized in maximum due to flower-like shape and alloyed formation with Ni. The Ni-Pd nanoflowers are ideally suited on electrochemical AOR while they have Calendula flower-like morphology and comparatively better alloyed formation property. The results prove that the Ni-Pd nanoflowers fabricated glassy carbon electrode (GCE) has superior electrocatalytic activity for AOR than that of PdNPs and Ni/Pd composite. This study will be of great interest and important for the development of low-cost Pd-based electrocatalysts.

Experimental

Synthesis of Ni-Pd nanoflowers, Ni/Pd composite and PdNPs.— The 28 mg (0.01 M eqv.) of Ni(NO3)2.6H2O and 10 ml of 0.08 M cetyltrimethylammonium bromide (CTAB) were mixed in a 20 ml vial by ultrasonic agitation (this solution was used as mediator), followed by the addition of 10 ml of K2PdCl4 (0.01 M) into the vial under stirring. Subsequently, the 5 ml of 0.01 M ascorbic acid (AA) was added as reductant. Thereafter, the solution was followed by heating in an oven at 65 °C for 4.5 h to produce an orange colored precipitate and black supernatant. The variation of Ni and Pd precursors had no effect in the nanoflower’s shape except much Pd clusters formation (Figure S1). The final product (Ni-Pd nanoflowers) was collected through centrifugation for three times using ethanol. Solubility of Ni-Pd nanoflowers had also been investigated in various solvents. For comparison, the Ni/Pd composite was prepared by a mixture of 0.01 M Ni and Pd solution together under stirring, followed by the addition of 10 ml of 0.08 M CTAB and added 5 ml of 0.01 M AA, respectively; then followed by the rest of the same procedure. The PdNPs were prepared with the same procedure excluding the adding of Ni precursor.

Characterization of physical parameters.— All transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDX) were taken by TECNAI model FI-20 (FEI, Netherlands), X-ray diffraction (XRD) spectra were carried out on a Rigaku D/max-2500, using filtered Cu Kα radiation. The X-ray photoelectron spectroscopic (XPS) measurements were performed on a Multilab...
suspension was prepared in ethanol (2 mg mL$^{-1}$) respectively was prepared by introducing a predetermined amount of the corresponding sample under sonication. For comparison, 10% Pd/C was prepared by introducing a predetermined amount of the Pd metal to the suspension. All electrochemical measurements were performed at room temperature in 1 M KOH aqueous solution, which were purged with high purity Ar for at least 30 min prior to each measurement.

**Electrochemical measurements.**— For the electrode preparation, Ni-Pd, Ni/Pd, and PdNPs suspension in water (1 mg mL$^{-1}$) separately was prepared by introducing a predetermined amount of the corresponding sample under sonication. For comparison, 10% Pd/C suspension was prepared in ethanol (2 mg mL$^{-1}$) with 10 μl of 5 wt% nafion in aliphatic alcohol). A 10 μl portion of the Ni-Pd, Ni/Pd, PdNPs or Pd/C suspension was then dropped onto the surface of a prepolished GCE, (0.3 cm in diameter) followed by dropping 5 μl of nafion solution (0.5 wt% in ethanol) as a binder (except in Pd/C electrode). All electrochemical measurements were taken using a three-electrode potentiostat [CHI 700C electrochemical workstation (USA)] in a grounded Faraday cage. A Pt wire and a calibrated Ag/AgCl electrode from Bioanalytical Systems Inc. (BAS) filled with 3 M NaCl solution were used as an auxiliary and reference electrode, respectively. All electrochemical measurements were performed at room temperature in 1 M KOH aqueous solution, which were purged with high purity Ar for at least 30 min prior to each measurement.

**Results and Discussion**

**Observation of nanoflower formation.**— In order to determine the nanoflower formation, we monitored the reaction at 1h, 2h, and 4.5h time points and nanoflower formation was investigated through the TEM analysis. The Figure 1 shows the growth process of Ni-Pd nanoflowers. At the beginning, the reduction of Pd ions into primary Pd nanocrystals upon AA addition in presence of CTAB, then the agglomeration of the primary Pd nanocrystals into intermediate agglomerates can be observed at the intermediate stage, and the isotropic growth of the agglomerates into flower-like nanostructures has found at the final stage. Finally, the cubic shaped NPs have turned into symmetrical spherical 3D nanoflowers shape by the agglomeration of Pd nanocrystals. By 4.5h, the conversion of Ni-Pd nanoflowers have completed. Here the Ni is acting as a mediator, Ni in CTAB helps to construct a nanoflower structure upon subsequent addition of Pd. It makes a composite with spherical shape when both Ni and Pd precursors are added together in CTAB (Figure S2). Furthermore, the Pd in CTAB is just NPs in shape.

**Characterization of Ni-Pd nanoflowers Ni/Pd composite and PdNPs.**— The Ni-Pd nanoflowers were first characterized using TEM. Figure 2 shows the TEM images of as prepared Ni-Pd nanoflowers. Figure 2a shows numerous Ni-Pd nanoflowers which have been obtained from the chemical synthesis. The well dispersed nanoflowers have a fairly uniform size of about 50 nm. Also this image shows that some of the Pd, instead of adding to the shell, nucleated to form small nanoclusters in the reaction solution, as observed in previous report.$^{28}$ A magnified TEM image (Figure 2b) shows a novel Calendula flower-like structure of a Ni-Pd nanoflower. The Pd petals are grafted on Ni seed with approximately 5–8 nm in diameter (outer part). The Pd petals are large and discrete. The high resolution TEM (HRTEM) image is indicating that the prepared Ni-Pd nanoflowers are entirely crystalline (Figure 2c). The lattice line spacing in petals are 0.223 and 0.229 nm, which are represented to Pd(111) and Ni(OH)$_2$ (101) plane, respectively,$^{26}$ and the encircled portions are probably the amorphous NiO.$^{33}$ The clear and prominent line spacing profile for Pd(111) plane can be seen in Figure 2c inset. The numerical analysis of Ni-Pd nanoflowers has done by EDS spectrum (Figure 2d), Pd and Ni were detected as 5.82 at% and 2.97 at% with C, O and N. Selected area electron diffraction (SAED) ring pattern (Figure 2d inset), which can be assigned to the diffractions from (111), (200), (220), and (311) planes of a face-centered cubic (fcc) Pd phase, respectively. Also, the line mapping of a single Ni-Pd nanoflower can be seen in Figure S2. For comparison, the TEM image of Ni/Pd composite can be seen in Figure S3.

The XRD patterns of Ni-Pd nanoflowers, Ni/Pd composite and PdNPs are shown in Figure 3 to characterize their crystal structure. Three characteristic typical peaks are observer in each pattern of Figure 3. The peaks at 2θ = 40.1°, 46.6° and 68.09° are assigned to the Pd (111), (200), and (220), respectively.$^{34}$ Nevertheless, the peaks at around 2θ = 44.7°, 54.3° and 76.3° corresponding to the Ni (111), (200) and (220) crystal planes were only observed in Ni-Pd nanoflowers XRD pattern which are similar to the other publication.$^{29}$ Comparatively smaller peaks at 2θ = 38.4°, 50.2° and 65° are representing...
Figure 3. The XRD patterns of Ni-Pd nanoflowers, Ni/Pd composite and PdNPs; inset: enlarged pattern around Pd(111) and Pd(200) peaks.

(111), (200) and (220) planes of NiO and/or Ni(OH)2, respectively, due to higher amount and alloyed formation,35 as already been observed in HRTEM image. Although, the PdNPs and Ni/Pd composite had not been observed any Ni or NiO peak due to absence of Ni in PdNPs and the fewer amount in Ni/Pd composite.32 Also, when Ni is in oxidized form it gives very small peak in XRD spectra due to amorphous nature.17,32 It is, however, the above mentioned Pd peaks are slightly shifted to higher angles in the Ni-Pd spectrum compared to PdNPs and Ni/Pd composite (Figure 3 inset). This shift indicates that Ni atoms which are around Pd sites had entered into the Pd lattice and forming a bimetallic transition zone.29

The average particle size was also calculated from Pd (220) peak by the Scherrer formula using equation Eq. 1:

$$d(\text{Å}) = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} [1]

where $k$ is a coefficient (0.9), $\lambda$ the wavelength of X-ray used (1.5406 Å), $\beta$ the full-width half maximum and $\theta$ is the angle at the position of peak maximum. The calculated sizes are ~47, ~41 and ~18 nm for Ni-Pd nanoflowers, PdNPs and Ni/Pd composite, respectively. Also, based on the same peak, the alloying percentages for Ni-Pd nanoflowers and Ni/Pd composite were calculated from the Vegard’s law33 and are presented in the Table I. The higher alloying% was found in Ni-Pd nanoflowers and was approximately 2 times than that of Ni/Pd composite. Thus the amount of Ni alloyed does not correspond to their nominal concentration which eventually supports that Ni is abundantly present in their oxide form in Ni-Pd nanoflowers.

| Material       | PdNPs | Ni/Pd | Ni-Pd | Pd/C |
|----------------|-------|-------|-------|------|
| Pd loading (μg cm⁻²) | 121.6 | 103.1 | 96.4  | 63.7 |
| Alloys formation (%) | - | 28.2  | 62.1  | -   |
| ECSA (m² g⁻¹) | 49    | 64    | 46    | 59   |
| Mass activity (j, mA m⁻²) | 266   | 236   | 966   | 268  |
| Stability after 200 cycles (%) | 16    | 59    | 25    | 18   |

The core level of Pd 3d and Ni 2p XPS spectra of Ni-Pd nanoflowers, Ni/Pd composite and PdNPs are shown in Figure 4. The XPS recorded signals from C (~285), O (~502), and N (~401.5) for all catalysts;18,36 with that attributable to Pd being the most significant and Ni 2p peaks were observed upon Ni addition (Figure S4). The C and N were appeared from organic compound CTAB. The Pd 3d spectrum of Ni-Pd nanoflowers (Figure 4a) shows two peaks for the 3d₅/₂ and 3d₃/₂ components at 336.3 and 341.7 eV, respectively, while those peaks are located at 335.7 and 341.1 eV for Ni/Pd composite and PdNPs (Figure 4a). Such positively shifted values are indicate that the Pd in Ni-Pd nanoflowers was present in a different electronic environment due to the alloyed formation.29,37 The Figure 4b shows the core level spectra of Ni 2p peaks, which shows a prominent peak at ~857 eV which is an indication of Ni was in oxidized form. Also, another three small peaks can be observed at 862.1, 874.2 and 880.1 eV that are attributed to the several oxo-Ni species, i.e., Ni(OH)₂, and NiOOH. As can be seen, all oxidized Ni peaks in Ni-Pd are positively shifted compared to the Ni/Pd and this shifts also suggested an alloyed formation of Ni-Pd nanoflowers. The Pd:Ni at% ratio was found as 2.6:1 and 1.5:1 for Ni/Pd and Ni-Pd, respectively. Indicating much amount of Ni is presents in Ni-Pd nanoflowers and most of them are in oxide and alloyed form.

Electrochemical investigation of Ni-Pd nanoflowers.— The electrochemical behavior of Ni-Pd nanoflowers, Ni/Pd composite, PdNPs and Pd/C were first investigated in Ar pursed 1 M KOH solution without and with 0.1 M ethanol, and are shown in Figure 5 separately (CVs with long range potential sweep can be seen in Figure S5). In Figure 5a, a couple of redox peaks can be observed for Ni-Pd nanoflowers in the forward (at around 0.39 V) and the backward (at around 0.32 V) directions, respectively. According to the Eq.2,32,38 both two peaks are attributed to the NiOOH transformation from Ni(OH)₂, similar CVs were observed in previous reports.39,40

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \hspace{1cm} [2]
\]
Also the redox peaks can be observed for Ni/Pd composite at positively shifted potential region but no any redox peaks were found in this potential region for PdNPs and Pd/C (O adsorption and desorption peaks to the Pd can be seen in negative potential region in Figure S5a). In further explanation, couple of redox peaks in Ni/Pd and Ni-Pd CVs, which are typical reversible reactions of Ni²⁺/Ni³⁺. However, for Ni-Pd nanoflowers obtained the highest peak current value among four catalysts, about 1.3 times higher than that of the Ni/Pd composite, indicating the nanoflower shape and the degree of alloy formation can enhance the activity of Ni-Pd electrode. Usually quasi-reversible peak can be observed for the Ni(OH)₂/NiOOH transformation on the surface of Ni due to iR drop. However, from the peak separation, current ratio and potential of the obtained peaks in Ni-Pd and Ni/Pd, it can be claimed that Ni(OH)₂/NiOOH transformation on the surface of Ni-Pd is better reversible. The electrochemical surface area (ECSA) of each catalyst was calculated by Eq. 3 with coulombic charge (Qo) for the reduction of PdO,

\[ ECSA = \frac{Q_o}{0.424} \]  

Where Qo is the surface charge that obtained from the area under forward scan, rather than caused by freshly chemisorbed species. This superior catalytic behavior may rise from two possible reasons. First, according to Eq. 4, the Ni(OH)₂ was formed during test and react with OH⁻ and/or (OH)ads, that facilitate to the EOR. Second, the excellent nanoflower structure of Ni-Pd that has higher degree of alloy formation with much amount of NiO. The magnitude of the peak in the forward scan is due to the oxidation of freshly chemisorbed species coming from the adsorption of EtOH; and the reverse oxidation peak is primarily associated with the removal of carbonaceous species that not completely oxidized in the forward scan, rather than caused by freshly chemisorbed species.

The ratio of the forward peak current density \( j_f \) and the backward peak current density \( j_b \), \( j_f/j_b \), is used to determine the Pd based catalyst’s tolerance to the intermediate carbonaceous species accumulated onto the electrode surface. Also higher value of \( j_f/j_b \) is attributed to more efficient oxidation of ethanol during the forward scan, and less accumulation of carbonaceous residues on the electrode surface. The \( j_f/j_b \) of Ni-Pd (1.17) was higher than that of Ni/Pd (1.14). This indicates that the electrode surface was less poisoned by adsorbed intermediates on the Ni-Pd catalyst. Moreover, the EOR in alkaline media goes through a dual-pathway mechanism. In the C₁ pathway, the C–C bonds break down and generate the strongly adsorbed COₐds and CH₂ads species. In the C₂ pathway, partially oxidation products such as acetaldehyde and acetate are produced due to the difficulty in breaking the C–C bond. Therefore, EOR on Ni/Pd would be the C₁ pathway and EOR on Ni-Pd would be the C₂ pathway while the higher \( j_f/j_b \) of Ni-Pd was observed in Ni-Pd. Additionally, as can be seen in Figure 5b inset, the forward scan CV curves exhibit that the Ni-Pd catalyst has better electrocatalytic activity for EOR, where the half-wave potential of the Ni-Pd catalyst was ca. 50 mV (at arrow marked region) negatively shifted compared to Ni/Pd catalyst. The onset potentials for both Ni-Pd and Ni/Pd were similar to the other reports in alkaline media.

Figure 6 shows the CVs of methanol (MeOH), EtOH, propanol (PrOH) and n-butanol (BuOH) oxidation on Ni-Pd nanoflowers modified electrode. The Ni-Pd electrocatalyst shows high activity for the EtOH oxidation in terms of the onset potential (\( E_{onset} \)) and peak current density than that of MeOH, BuOH and PrOH, respectively, in 1 M KOH aqueous solution with 0.1 M of respective alcohols. Comparatively shorter chain alcohols (EtOH and MeOH) are better catalyzed than that of longer chain (BuOH and PrOH) on Ni-Pd electrocatalyst. However, the catalytic behaviors of EtOH and MeOH have been investigated by several groups via CVs and EtOH was more favorable (in respect to the current density and \( E_{onset} \)) than MeOH for electrocatalysis. We also had found the same phenomena for EtOH and MeOH. Also, the same behavior had observed for BuOH and PrOH. Most probably, the even carbon number have some influence on higher catalysis for AOR. The CV curves for AOR show two peaks

\[ \text{Pd–(CH₃COO)}_{\text{ads}} + \text{SOH}^- \rightarrow \text{NiOOH} + \text{EtOH} + \text{NiOOH} \rightarrow \text{Pd–CH₃COO}^- + 4\text{H₂O} + 4e^- \]
Figure 6. The CVs of Ni-Pd recorded in 1 M KOH electrolyte with 0.1 M alcohol at a scan rate of 50 mV s$^{-1}$; inset: the magnified CVs at the cited potentials.

The CVs located around 0.35 and 0.55 V in the positive scan. According to previous report, the first peak (inset) from the partial reaction current for carbonate formation (in alkaline condition), and the second peak is mainly attributed to the acetate formation (in alkaline condition). This dual-peak characteristic indicates that the small amount of carbonate formation on the Ni-Pd while it is considerable when the lower concentration of alcohol is used. According to the peak intensity, the highest amount of carbonate was produced from MeOH than that of other alcohols.

The kinetic comparison for all alcohols on Ni-Pd nanoflowers.— The concentration dependent potentiodynamic measurements of the AOR on the Ni-Pd catalyst in Ar saturated 1 M KOH solution have been investigated (Figure 7). As observed, with the increasing of alcohol concentration, the $E_{\text{onset}}$ was shifted to the negative direction and give rise to a peak with higher current density for AOR. Nevertheless, the half wave potentials ($E_{1/2}$) were shifted toward positive direction in the order of MeOH > BuOH > PrOH except EtOH (the $E_{1/2}$ was linear in all concentration). Indicating the Tafel slopes are also increasing. The higher Tafel slope is the indication of lower charge-transfer kinetic on the electrode surface, while, it is not preferable. Therefore, better catalysis with low poisoning can be observed for EtOH than for other alcohols. Moreover, significantly lower carbonate production was observed toward EtOH than that of MeOH, and no carbonate production peak was observed for BuOH and PrOH at higher concentration on Ni-Pd modified electrodes.

For better kinetic analysis, three important parameters can be compared in here, the $j/j_b$ ratio (a) peak potential shift (b) and Tafel plots (c) for AOR at Ni-Pd modified electrodes are displayed in Figure 8. There are some significant observations involved in the experiment: first, as can be seen in Figure 8a, the $j/j_b$ ratios are distributed as an umbrella-like with respect to the concentration of alcohols and all values are more than 1. However, at the high concentration, the curve lines are dropped at BuOH, PrOH, MeOH and comparatively straight line can be seen at EtOH. Also, according to the curve line slope, much curved line can be found at BuOH, PrOH, MeOH, and EtOH, respectively. Indicating, poisoning tolerance increased in the order of BuOH > PrOH > MeOH > EtOH. Second, as can be seen in Figure 8b, the peak potentials are shifted to the higher potential with respect to the higher concentration of alcohols. The variation of peak potential with the increasing of alcohol concentration is strongly related to the uncompensated resistance ($R_u$) in the test system. According to the straight line slope, higher rate of peak potential shift can be found at BuOH, PrOH, MeOH, and EtOH, respectively. Indicating, $R_u$ decreased in the order of BuOH > PrOH > MeOH > EtOH. Third, Figure 8c shows the Tafel plots (kinetic current density as a function of potential) at linear region of forward scan for 0.1 M alcohol in 1 M KOH at a scan rate of 50 mV s$^{-1}$ on Ni-Pd catalyst. As the potential is further increased...
above 0.5 V, the Tafel plot becomes curved, indicating the AOR is no longer charge transfer controlled reactions. Tafel slopes are derived from the linear region and the slopes are 164, 169, 190, 201 mV dec$^{-1}$ for EtOH, MeOH, BuOH and PrOH electrooxidation, respectively, which are reasonable for Ni and Pd containing electrocatalysts. The lower Tafel slope indicates the faster charge-transfer kinetics of electrocatalysis and the order of faster charge-transfer kinetic is EtOH > MeOH > BuOH > PrOH in the alkaline medium.

The stability of Ni-Pd nanoflowers, Ni/Pd composite, PdNPs, and Pd/C were investigated by the long-term CV sweep up to 200 cycles in 0.5 M ethanol containing 1 M KOH solution. The plot of forward peak current density vs. cycle number is shown in Figure 9. From Figure 9, we conclude that the activity order of AOR (here EOR) in term of the relative current is Ni-Pd > Ni/Pd > Pd/C > PdNPs. Particularly, the stability of Ni-Pd catalyst in terms of relative current is more than 3.5 times higher than Pd/C, and PdNPs after 200 cycles (Figure 9 inset). The indicates superior efficiency and poisoning tolerance on Ni-Pd than that of other tested catalysts.

Conclusions

In summary, we successfully made Ni-Pd nanoflowers via a simple wet chemical method and introduced to the AOR with superior catalytic activity than Ni/Pd composites PdNPs and Pd/C. The combined characterization techniques suggested that the Ni-Pd nanoflowers have high degree of alloyed formation and Ni is in oxidized form. The Ni-Pd catalyst demonstrated higher peak current density, mass activity and much poison free electrode surface via CV for AOR in alkaline solution. Also it showed superior long-term stability compared to the Ni/Pd composites, PdNPs and Pd/C. The kinetic study between four monohydric shorter carbon chain containing alcohols revealed that the unique nanostructure and higher degree of alloy formation lead to the higher charge transfer rate with less poisoning in the order of EtOH > MeOH > BuOH > PrOH during AOR at Ni-Pd. We hope that this report will encourage to preparing Ni based nanoflowers for Pt free catalyst preparation and application in FCs including DEFCs.

Acknowledgment

This research has supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010–0007864).

References

1. Z. Yin, H. Zheng, D. Ma, and X. Bao, J. Phys. Chem. C, 113, 1001 (2009).
2. X. Chen, Z. Cai, and X. Chen, and M. Oyama, J. Mater. Chem. A, 2, 315 (2014).
3. L. Shi, A. Wang, T. Zhang, B. Zhang, D. Su, H. Li, and Y. Song, J. Phys. Chem. C, 117, 12526 (2013).
B. Y. Xia, H. B. Wu, X. Wang, and X. W. Lou,
19. C. Cui, L. Gan, H.-H. Li, S.-H. Yu, M. Heggen, and P. Strasser,
23. E. Lee, M. S. Ahmed, J.-M. You, S. K. Kim, and S. Jeon,
13. E. Lee, M. S. Ahmed, J.-M. You, S. K. Kim, and S. Jeon,
14. M. S. Ahmed and S. Jeon, J. Power Sources, 255, 157 (2014).
11. D.-J. Guo, S.-K. Cui, D. Cheng, P. Zhang, L. Jiang, and C.-C. Zhang, J. Power Sources, 195, 1001 (2010).
12. M. S. Ahmed and S. Jeon, J. Power Sources, 215, 168 (2012).
13. E. Lee, M. S. Ahmed, J.-M. You, S. K. Kim, and S. Jeon, Thin Solid Films, 520, 6664 (2012).
14. M. S. Ahmed and S. Jeon, J. Nanosci. Nanotechnol, 13, 306 (2013).
15. H. Xu, L.-X. Ding, C.-L. Liang, Y.-X. Tong, and G.-R. Li, NPG Asia Mater, 5, e69 (2013).
16. M. S. Ahmed, D. Kim, and S. Jeon, Electrochim. Acta, 92, 168 (2013).
17. S. Y. Shen, T. S. Zhao, J. B. Xu, and Y. S. Li, J. Power Sources, 195, 1001 (2010).
18. M. S. Ahmed and S. Jeon, J. Power Sources, 218, 168 (2012).
19. C. Cui, L. Gan, H.-H. Li, S.-H. Yu, M. Heggen, and P. Strasser, Nano Lett., 12, 5885 (2012).
20. B. Y. Xia, H. B. Wu, X. Wang, and X. W. Lou, J. Am. Chem. Soc., 134, 13934 (2012).
21. L. Zhang, N. Li, F. Gao, L. Hou, and Z. Xu, J. Am. Chem. Soc., 134, 11326 (2012).
22. M. S. Ahmed, J.-M. You, H. S. Han, D.-C. Jeong, and S. Jeon, J. Nanosci. Nanotechnol, 14, 5722 (2014).
23. A. B. Delpeuch, T. Asset, M. Chatenet, and C. Cremers, J. Electrochem. Soc., 161, F918 (2014).
24. Y. Wang, Y. Zhao, J. Yin, M. Liu, Q. Dong, and Y. Su, Int. J. Hydrogen Energy, 39, 10111 (2014).
25. L.-X. Ding, A.-L. Wang, Y.-N. Ou, Q. Li, R. Guo, W.-X. Zhao, Y.-X. Tong, and G.-R. Li, Sci. Rep., 3, 1181 (2013).
26. M. S. Ahmed and S. Jeon, ACS Catal., 4, 1830 (2014).
27. D. Diabate, T. W. Napporn, K. Servat, A. Habrionx, S. Arri-Clacons, A. Trokourey, and K. B. Kokoh, J. Electrochem. Soc., 160, H302 (2013).
28. S. T. Nguyen, D. S. L. Tan, J.-M. Lee, S. H. Chan, J. Y. Wang, and X. Wang, Int. J. Hydrogen Energy, 36, 9645 (2011).
29. M. Zhang, Z. Yan, and J. Xie, Electrochim. Acta, 77, 237 (2012).
30. H. Gokou, S. F. Ho, O. Metin, K. Korkmaz, A. M. Garcia, M. S. Gultekin, and S. Sun, ACS Catal., 4, 1777 (2014).
31. U. B. Demirci, J. Power Sources, 173, 11 (2007).
32. Z. Zhang, L. Xin, K. Sun, and W. Li, Int. J. Hydrogen Energy, 36, 12686 (2011).
33. A. Dutta and J. Dutta, J. Mates Chem., A, 2, 3237 (2014).
34. D. Kim, M. S. Ahmed, and S. Jeon, J. Mater Chem., 22, 16353 (2012).
35. J.-H. Kim, S. H. Kang, K. Zhu, J. Y. Kim, N. R. Neale, and A. J. Frank, Chem, Commun., 47, 5214 (2011).
36. M. S. Ahmed, H. S. Han, and S. Jeon, Carbon, 61, 164 (2013).
37. N. J. S. Costa, M. Guerrero, V. Colliere, E. Teixeira-Neto, R. Landers, K. Philippot, and L. M. Rossi, ACS Catal., 4, 1735 (2014).
38. H. B. Hassan and Z. Abdel Hamid, Int. J. Hydrogen Energy, 36, 849 (2011).
39. M. Zhou, P. Xiao, W. Guo, J. Deng, F. Liu, and Y. Zhang, J. Electrochem. Soc., 161, H133 (2014).
40. S.-J. Zhang, Y.-X. Zheng, L.-S. Yuan, and L.-H. Zhao, J. Power Sources, 247, 428 (2014).
41. A. Rahim, R. Abdel Hameed, and M. Khalil, J. Power Sources, 134, 160 (2004).
42. K. Lee, S. W. Kang, S.-U. Lee, K.-H. Park, Y.W. Lee, and S. W. Han, ACS Appl. Mater Interfaces, 4, 4208 (2012).
43. N. A. M. Barakat, M. Motlak, A. A. Elzatahry, K. A. Khalil, and E. A.M. Abdelghani, Int. J. Hydrogen energy, 39, 305 (2014).
44. Y. Zhao, L. Zhan, J. Tian, S. Nie, and Z. Ning, Electrochim. Acta, 56, 1967 (2011).
45. S. C. S. Lai, S. E. F. Kleijn, F. T. Z. Ozturk, V. C. van Rees Vellinga, J. Koning, R. Rodriguez, and M. T. M. Koper, Catal. Today, 154, 92 (2010).
46. H. Yang, H. Wang, H. Li, S. Ji, M. W. Davids, and R. Wang, J. Power Sources, 260, 12 (2014).
47. L. Ma, H. He, A. Hsu, and R. Chen, J. Power Sources, 241, 696 (2013).
48. R. N. Singh and R. Awasthi, Catal. Sci. Technol., 1, 778 (2011).
49. L. Jiang, A. Hsu, D. Chu, and R. Chen, Int. J. Hydrogen Energy, 35, 365 (2010).
50. Z.-Y. Zhou, Q. Wang, J.-L. Lin, N. Tian, and S.-G. Sun, Electrochim. Acta, 55, 7995 (2010).
51. M. S. Ahmed, H. Jeong, J.-M. You, and S. Jeon, Electrochim. Acta, 56, 4924 (2011).
52. M. S. Ahmed, D. Kim, H. S. Han, H. Jeong, and S. Jeon, J. Nanosci. Nanotechnol, 12, 8349 (2012).