

HYDROGEN GENERATION BY HYDROLYSIS OF NaBH_4 WITH EFFICIENT Co-La-W-B CATALYST FOR PEM FUEL CELLS

A. EKİNCİ^a, S. HOROZ^{b,*}, O. BAYTAR^c, Ö. ŞAHİN^c

^a*Department of Occupational Health and Safety, Siirt School of Health, Siirt University, 56100 Siirt, Turkey*

^b*Department of Electrical and Electronics Engineering, Faculty of Engineering, Siirt University, 56100 Siirt, Turkey*

^c*Department of Chemical Engineering, Faculty of Engineering, Siirt University, 56100 Siirt, Turkey*

In this study, Co-B based quaternary alloy catalysts were synthesized for use in NaBH_4 hydrolysis. Lanthanum (La) and tungsten (W) metals were added to Co-B catalyst by chemical reduction method. The effect of metal content (La and W), NaBH_4 concentration, NaOH concentration, catalyst amount and temperature parameters were investigated in NaBH_4 hydrolysis. Activity results show that the hydrolysis reaction rate first increases and then decreases with increasing NaBH_4 concentration as well as NaOH concentration. The activation energy of the hydrolysis for Co-La-W-B catalysts was calculated as 39.2 kJ / mol. The maximum value of hydrogen generation rate was 3280 ml / min. In terms of application, hydrogen produced in the presence of the Co-La-W-B catalyst was used in PEM fuel cell application. Average yield value according to power and ideal voltage and maximum power value of the system were determined as 57%, 73% and 1.4 Watt, respectively. This original study demonstrates that the Co-La-W-B catalyst can be used as an ideal catalyst for PEM fuel cell applications.

(Received January 30, 2020; Accepted April 5, 2020)

Keywords: Application, Catalyst, Hydrolysis, PEM, Synthesis

1. Introduction

Alternative energy sources have been on the agenda of the scientific world for a long time. The most basic characteristics of an alternative energy source can be listed as being less harmful to the environment, renewable and cost-effective. In this sense, proton exchange membrane fuel cell (PEMFC) and hydrogen energy are one of these alternatives [1]. PEM fuel cells, whose total efficiency can reach up to 80%, are also known as continuous-running batteries. On the other hand, it is also possible to use hydrogen gas as a direct fuel without any intermediate process and energy requirements [2]. The technique of generating hydrogen in situ is one of the key issues for the commercialization of PEMFC. Recently, hydrogen gas formation by catalyzing alkaline solutions from the NaBH_4 compound has proved to be a method of producing hydrogen for PEMFC [3]. Furthermore, the by-product NaBO_2 is environmentally clean and can be recycled to re-synthesize that NaBH_4 [4].

Therefore, NaBH_4 hydrolysis is considered to be an efficient and environmentally friendly hydrogen production method and is gaining increasing attention. Catalysts are an important issue for the sustainable supply of hydrogen from NaBH_4 hydrolysis [5-8]. In recent years, important research has focused on non-noble metal catalysts, given the high cost and low weldability. Both cobalt (Co) and nickel (Ni) based catalysts show good behavior and recyclability in alkali NaBH_4 solution [9]. Co and Ni are primarily regarded as elite candidates to serve this purpose [10]. Non-noble metals perform better when used only in boride forms, because boron can protect active metal regions from oxidation by electron transfer [11]. In the presence of Co – B [12], Co-Ni – B [13], Co-W – B [14], Co-Ni – P – B [15], Co-Cr – B [16] and some other catalysts, it has also been found to accelerate the rate of hydrogen from hydrolysis of NaBH_4 . The inclusion of transition

* Corresponding author: sabithoroz@siirt.edu.tr

metal elements such as Fe, Cu, Cr, Mo and W to improve the properties of the catalyst has been recognized in many previous studies [17]. These transition metals generally become an atomic barrier to prevent the accumulation of alloy catalyst [18].

In this study, Co-La-W-B catalyst was synthesized. The structure of the Co-La-W-B catalyst and the effects of reaction conditions such as NaBH_4 and NaOH concentrations, reaction temperature and catalyst amount in NaBH_4 catalytic hydrolysis were also investigated. The values that the catalyst showed at optimum optimum conditions were used in single cell PEM fuel cell application with Pt / C catalyst support. At the same time, the power and yield of the fuel cell were evaluated with hydrogen produced from NaBH_4 hydrolysis catalyzed in the presence of the Co-La-W-B catalyst.

2. Materials and methods

2.1. Catalyst synthesis

In this study, Co-La-W-B catalyst which has not been used previously in NaBH_4 hydrolysis was synthesized by chemical precipitation and reduction method. Detailed production of the catalyst is given below.

A certain amount of lanthanum hexahydrate, cobalt chloride hexahydrate and tungsten nitrate were mixed in 100 mL of purified water. The prepared metal mixture was left in an ice bath to ensure that the temperature was in the range of 0-5 °C. Then a certain amount of NaBH_4 solution prepared in 50 mL of purified water was added dropwise onto the metal mixture. The resulting black precipitate was washed several times with distilled water and ethanol to remove impurities. The synthesized Co-La-W-B catalyst was dried at 100 °C under N_2 gas. The resulting catalyst was stored in a closed container for use in NaBH_4 hydrolysis.

2.2. NaBH_4 hydrolysis

The resulting catalyst was used in hydrolysis of NaBH_4 . Conditions used to perform NaBH_4 hydrolysis experiments were 10 mL solution volume, 25 mg catalyst amount and 2.5% NaBH_4 concentration. The graphs of hydrogen volume-time obtained as a result of NaBH_4 hydrolysis were plotted using cumulative method. The effect of different parameters such as metal ratio (La/W), NaOH concentration, NaBH_4 concentration, catalyst amount and temperature were investigated. Finally, the activation energy was calculated by determining the decomposition kinetics of NaBH_4 in the presence of Co-La-W-B catalyst.

3. Results and discussion

3.1. NaBH_4 hydrolysis

3.1.1. Effect of W concentration on hydrogen generation rate

To increase the activity of Co-B and Co-La-B catalysts previously used in NaBH_4 hydrolysis, W was attached to these catalysts. The graph of time vs hydrogen generation yield for Co-B, Co-La-B, Co-W-B and Co-La-W-B catalysts is given in Fig. 1.

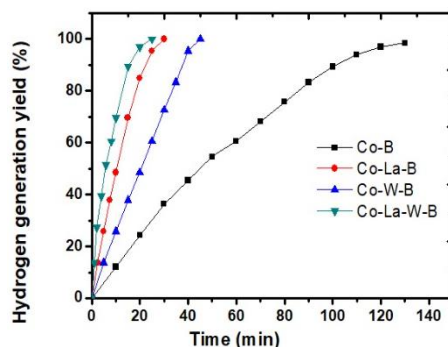


Fig. 1. The graph of time vs hydrogen generation yield for Co-B, Co-La-B, Co-W-B and Co-La-W-B catalysts.

As can be clearly seen from Fig. 1, W metal increases the activity of the Co-La-B catalyst. NaBH_4 hydrolysis is completed for 140 minutes in the presence of Co-B catalyst, while it is completed for 22 minutes in the presence of Co-La-W-B catalyst. Thus, it was observed that W metal increased the activity of Co-B catalyst 7 times.

To investigate the effect of W concentration on catalytic activity, the Co-La-W-B amorphous catalysts were synthesized by varying the concentration of W between 1% and 10%, keeping the Co / (Co + La) molar ratio constant at 0.85. The graph of time vs hydrogen generation yield for Co-La-W-B catalysts with different W concentrations is given in Figure 2a. In addition, the graph of W concentration vs. hydrogen generation rate is given in Fig. 2b.

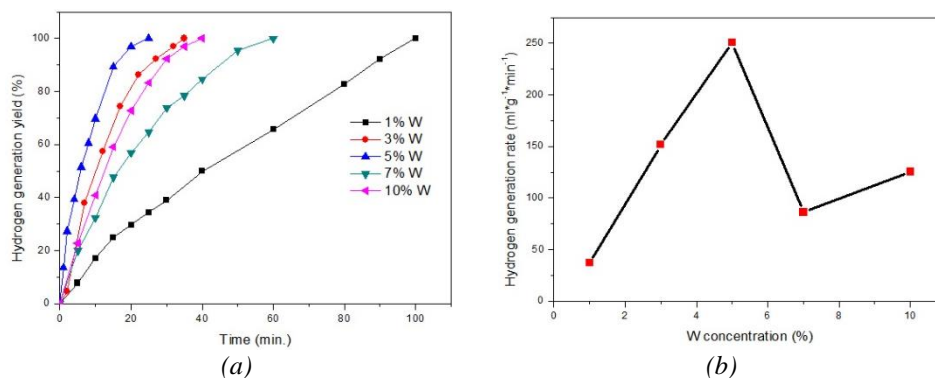


Fig. 2. (a). The graph of time vs hydrogen generation yield for Co-La-W-B catalysts with different W concentrations; (b). The graph of W concentration vs. hydrogen generation rate.

As can be seen from Fig. 2b, it was realized that when the W concentration was increased from 1% to 5%, the hydrogen generation rate increased and then decreased. This is likely due to the low number of catalyst active sites when the concentration W is 1% but high when the concentration is 5%. Thus, the best tungsten concentration was determined as 5%.

3.1.2. Effect of catalyst amount on hydrogen generation rate

NaBH_4 hydrolysis experiments were carried out using different amounts of catalyst to examine the effect of Co-La-W-B catalyst amount on hydrogen generation yield. The graph of time vs hydrogen generation yield for Co-La-W-B catalysts with different catalyst amounts is given in Figure 3a. In addition, the graph of catalyst amount vs. hydrogen generation rate is given in Figure 3b.

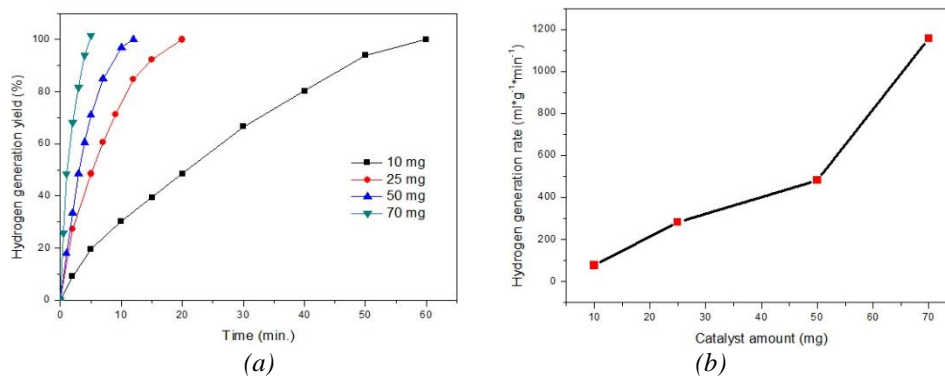


Fig. 3. (a) The graph of time vs hydrogen generation yield for Co-La-W-B catalysts with different catalyst amounts; (b) The graph of catalyst amount vs. hydrogen generation rate.

As can be seen from both figures, as the amount of catalyst increases, both hydrogen generation yield and hydrogen generation rate increase. This is likely due to the increase in the number of active sites in the structure of the catalyst with the amount of catalyst. This result shows that hydrogen generation from NaBH_4 in the presence of Co-La-W-B catalyst is catalyst controlled.

3.1.3. Effect of NaOH concentration on hydrogen generation rate

NaBH_4 hydrolysis experiments were performed in the presence of different NaOH concentrations and the graph of time vs hydrogen generation yield for Co-La-W-B catalysts in the presence of different NaOH concentrations and the graph of NaOH concentration vs. hydrogen generation rate are indicated in Fig. 4a and Fig. 4b, respectively.

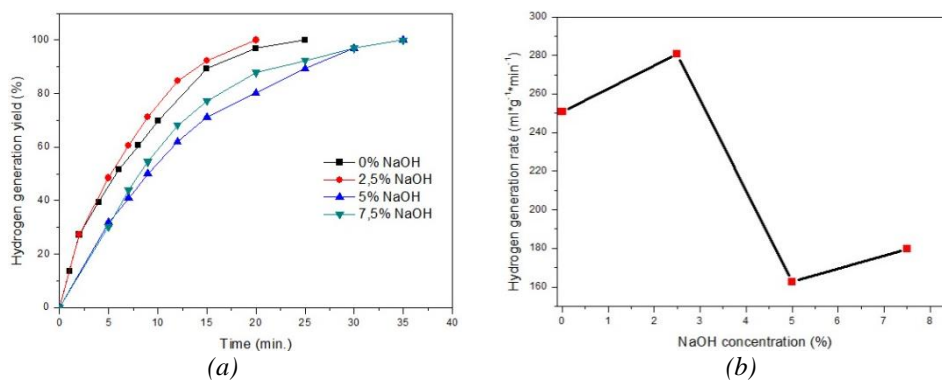


Fig. 4. (a) The graph of time vs hydrogen generation yield for Co-La-W-B catalysts in the presence of different NaOH concentrations; (b) The graph of NaOH concentration vs. hydrogen generation rate.

When the NaOH concentration is 2.5%, hydrogen generation rate increases and then decreases. This is likely due to the presence of excess hydroxyl ion in the solution medium in the hydrolysis of NaBH_4 . Because hydroxyl ions form a strongly complex water, the free water needed for hydrolysis of NaBH_4 is reduced [3]. Ding et al. [19] found the same results for the Co-Cu-B catalyst used in hydrolysis of NaBH_4 . They indicated that an appropriate increase in NaOH concentration could accelerate the hydrolysis of catalyzed NaBH_4 and increase the rate of hydrogen generation, since the OH^- ion is involved in the hydrolysis of NaBH_4 . Moreover, the authors stated that excessive NaOH concentration would lead to reduced NaBO_2 solubility followed by precipitation after solution and adhesion to the catalyst surface.

3.1.4. Effect of NaBH_4 concentration on hydrogen generation rate

The effect of NaBH_4 concentration on the hydrogen generation rate is the key point of the kinetic study. To examine this, experiments were performed at different NaBH_4 concentrations (1, 2.5, 5, and 7.5% by weight). The graph of time vs hydrogen generation yield for Co-La-W-B catalysts in the presence of different NaBH_4 concentrations and the graph of NaBH_4 concentration vs. hydrogen generation rate are indicated in Fig. 5a and Fig. 5b, respectively.

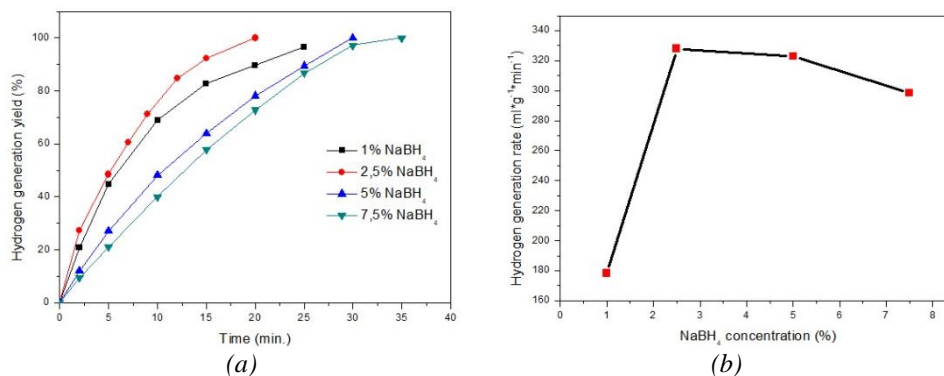


Fig. 5. (a) The graph of time vs hydrogen generation yield for Co-La-W-B catalysts in the presence of different NaBH_4 concentrations; (b) The graph of NaBH_4 concentration vs. hydrogen generation rate.

When the NaBH_4 concentration increases from 1% to 2.5%, the hydrogen generation rate increases and then decreases. The probable cause of this is the effect of mass and heat transfer during the reaction. However NaBO_2 concentration increases with increasing NaBH_4 concentration solution and this leads to an increase in solution viscosity [20]. When the NaBH_4 concentration is 2.5%, it is clear that the hydrogen generation rate is maximum. Similar results was observed by Liu et al. [21]. The increase in viscosity does not lead to limitations of mass transfer only from the NaBH_4 solution to the inner surface of the catalysts. At the same time, NaBO_2 concentration may exceed the solubility limit. NaBO_2 can precipitate and inhibit the active site on the catalyst surface. Thus, it prevents contact of BH_4 and subsequent hydrolysis rate [22]. The hydrogen generation rate depends on the competition between the effects of mass transfer and heat transfer. When the NaBH_4 concentration is less than 10% by weight, the hydrogen generation rate can be controlled by heat transfer since the viscosity of the solution is low and the mass transfer limitation is also relatively poor.

3.1.5. Effect of temperature on hydrogen generation rate

Hydrolysis of NaBH_4 is temperature sensitive. Therefore, five different temperatures were selected to investigate the activation energy of NaBH_4 hydrolysis. Fig. 6 indicates the graph of time vs hydrogen generation yield for Co-La-W-B catalysts at different temperatures.

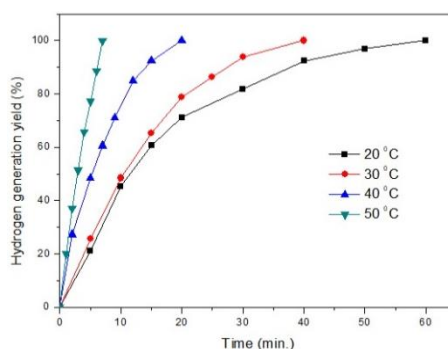


Fig. 6. The graph of time vs hydrogen generation yield for Co-La-W-B catalysts at different temperatures.

It was observed that the hydrolysis experiment at 30 °C was completed in 40 min while the same experiment was completed in 7 min at 50 °C. It is well known that the rate of BH_4^- ions in the solution increases with increasing temperature. Thus, this situation is thought to have a positive effect on the rate of hydrolysis. One of the main reasons for measuring the gait of any reaction at different temperatures is the determination of the reaction rate constant and the corresponding activation energy required to carry out the reaction.

According to the Arrhenius equation is given in Equation (1)

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (1)$$

where, The k is hydrogen generation rate, A ; preexponential factor, E_a ; the activation energy as kJ mol^{-1} , R ; ideal gas constant as $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and T ; is the solution temperature as $^{\circ}\text{K}$.

In order to determine the activation energy using Arrhenius equation, $(1 / T)$ vs $\ln(k)$ is plotted as shown in Fig. 7.

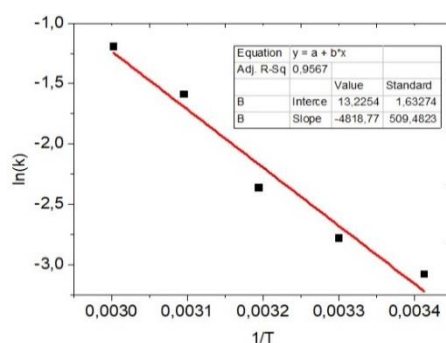


Fig. 7. The graph of $(1 / T)$ vs $\ln(k)$.

According to the graph, the activation energy of the Co-La-W-B catalyst was calculated as 39.2 kJ mol^{-1} . In general, the obtained activation energy for Co-La-W-B catalyst is much lower than the reported results in the literature [7, 12, 23, 24]. As a result, it can be said that the synthesized quaternary Co-La-W-B catalyst has higher catalytic activity compared to other catalysts.

3.2. PEM Fuel Cell Applications

The hydrogen produced using the synthesized Co-La-W-B catalyst was used in the PEM fuel cell application. Current, voltage and power generation values were measured at specific time intervals using a constant charge amount (10 ohms). The open circuit voltage for the single-cell PEM fuel cell was measured as 0.9 volts. Time-voltage (Figure 8), time- current (Fig. 9) and current-voltage-power (Fig. 10) graphs were obtained from the measurements. Average yield value according to power and ideal voltage were determined as 57% and 73%, respectively.

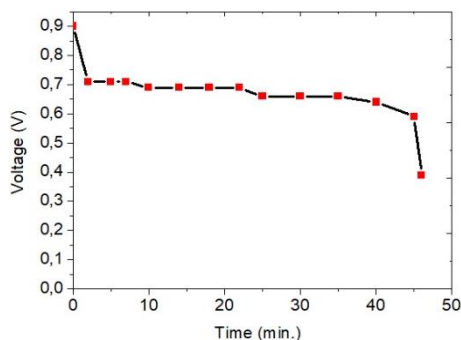


Fig. 8. The graph of time vs voltage for a PEM fuel cell.

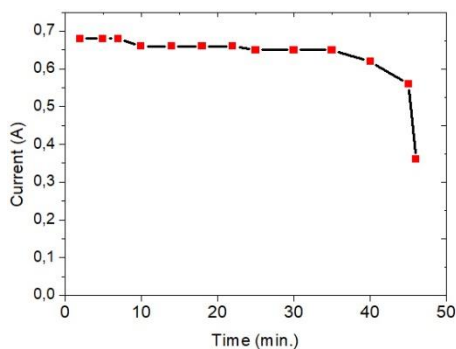


Fig. 9. The graph of time vs current for a PEM fuel cell.

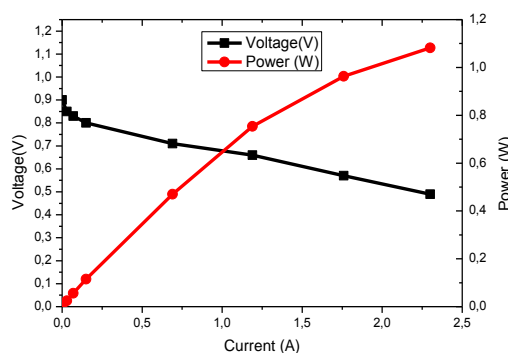


Fig. 10. The graph of current-voltage-power for a PEM fuel cell.

4. Conclusions

NaBH₄ hydrolysis experiments were performed in the presence of amorphous Co-La-B-W catalyst. It has been experimentally observed that the catalytic activity of the Co-La-B-W catalyst is higher than the Co-B, Co-La-B and Co-W-B catalysts. The effect of W metal ratio, NaBH₄ concentration, NaOH concentration, catalyst amount and temperature parameters were investigated in NaBH₄ hydrolysis experiments. The possible reasons why the activity of the Co-La-W-B catalyst is high are listed below;

1) large active surface area 2) better absorption of OH⁻ group ions in the presence of catalyst 3) synergistic effects caused by mixing each chemical element in the catalyst in a well defined ratio.

It was observed that the increase in temperature had a positive effect on hydrogen generation rate. The value of activation energy from the Arrhenius equation was calculated as 39.2 kJ mol⁻¹. The hydrogen produced using the synthesized Co-La-W-B catalyst was used in the PEM fuel cell application. Average yield value according to power and ideal voltage and maximum power value of the system were determined as 57%, 73% and 1.4 Watt, respectively. This original study demonstrates that the Co-La-W-B catalyst can be used as an ideal catalyst for PEM fuel cell applications.

References

- [1] A. L. Dicks, Journal of Power Sources **61**(1), 113 (1996).
- [2] O. Baytar et al., Digest Journal of Nanomaterials and Biostructures **14**(3), 673 (2019).
- [3] M.S.İzgi et al., Digest Journal of Nanomaterials and Biostructures **14**(4), 1005 (2019).
- [4] B. H. Liu et al., International Journal of Hydrogen Energy **33**(4), 1323 (2008).
- [5] O.Baytar, Acta Chimica Slovenica **65**(2), 407 (2018).

- [6] M.S. İzgi et al., *Journal of the Institute of Science and Technology* **7**(4), 151 (2017).
- [7] N. Patel, R. Fernandes, A. Miotello, *Journal of Catalysis* **271**(2), 315 (2010).
- [8] C. Wu et al., *Materials Letters* **59**(14), 1748 (2005).
- [9] A. Ekinçi et al., *Journal of Materials Science: Materials in Electronics* **31**(2), 1210 (2020).
- [10] S. Nar et al., *Chalcogenide Letters* **15**(10), 491 (2018).
- [11] A. Ekinçi et al., *Journal of Materials Science: Materials in Electronics* **29**(6), 5233 (2018).
- [12] R. Kadrekar et al., *Applied Surface Science* **518**(1), 146199 (2020).
- [13] Y. Wei et al., *International Journal of Hydrogen Energy* **42**(9), 6072 (2017).
- [14] C. Li et al., *Journal of colloid and interface science* **524**, 25 (2018).
- [15] R. Fernandes, N. Patel, A. Miotello, *Journal of Hydrogen Energy* **34**, 2893 (2009).
- [16] Y. Chen, H. Jin, *Journal of Materials Research* **35**(3), 281 (2020).
- [17] A. Ekinçi et al., *Journal of Non-Oxide Glasses* **10**(3), 71 (2018).
- [18] Y. Zhao et al., *Journal of Power Sources* **207**, 120 (2012).
- [19] X.-L. Ding et al., *International Journal of Hydrogen Energy* **35**(20), 11077 (2010).
- [20] P. Krishnan et al., *Journal of Power Sources* **143**(1), 17 (2005).
- [21] C.-H. Liu et al., *Applied Catalysis B: Environmental* **91**(1), 368 (2009).
- [22] Y. C. Zou et al., *Journal of Hydrogen Energy* **36**(19), 12343 (2011).
- [23] J. Chang, F. Du, *Advanced Materials Research* **724-725**, 735 (2013).
- [24] H.-B. Dai et al., *Journal of Power Sources* **195**(1), 307 (2010).