

The modification of anode material for direct borohydride fuel cell

Małgorzata Graś¹ · Agnieszka Sierczyńska² · Katarzyna Lota² ·
Ilona Acznik² · Grzegorz Lota^{1,2}

Received: 21 June 2016 / Revised: 27 October 2016 / Accepted: 31 October 2016 / Published online: 12 November 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

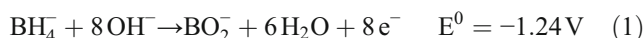
Abstract The direct borohydride fuel cell (DBFC) is a promising device that converts chemical energy into electricity by electrochemical reactions. This type of power source is technically more simple than traditional fuel cells, because it does not require any hydrogen container and noble metals. Hydrogen evolution during hydrolysis can be inhibited by modification of anode materials. Extensive studies are focused on various specific electrocatalysts and their impact on oxidation and hydrolysis of borohydride. The aim of the study is to determine the effect of anode material composition using borohydride as a fuel. In order to enhance the utilization of borohydride fuel, AB₅-type alloy (LaMnNi_{3.55}Al_{0.30}Mn_{0.40}Co_{0.75}) was modified by adding Si or two kinds of carbon materials using the ball milling method. The most proper electrolyte was selected. The physical and electrochemical properties of anode materials were evaluated by scanning electron microscopy (SEM), cyclic voltammetry, chronopotentiometric measurements and electrochemical impedance spectroscopy. Studies showed that graphite was the best additive to anode material due to its density, compact structure and improvement of conductivity.

Keywords Direct borohydride fuel cell · AB₅ alloy · Anode composition · Borohydride electrolyte

Introduction

Rapid technological development increases a tendency to develop power sources which can deliver enough power and possess adequate lifespan for the next generation of portable electronic devices. Direct borohydride fuel cell (DBFC) can be used as an alternative system for them [1]. Fuel cells are quiet, efficient and environmentally safe energy devices that directly convert chemical energy into electricity [2]. Borohydride as a solid fuel is more convenient to store and transport than hydrogen; moreover, it is chemically stable and non-flammable. The only products of the reaction (3) are water and borate ion, which are relatively easy to recycle back to borohydride [3, 4]. Sources of hydrogen could be LiBH₄, NaBH₄ or KBH₄. The sodium compounds are cheaper and have a lower molar mass, while the potassium compounds have a higher conductivity. Sodium borohydrides contain 10.6 wt.% of hydrogen and provide a high specific capacity of 5.6 Ah g⁻¹. Theoretically, borohydrides are able to release 8 e⁻ from one molecule.

Fuel is oxidised directly at the anode:



Oxygen reduction at the cathode:

(The oxidant could be oxygen, air or hydrogen peroxide).



Total reaction:



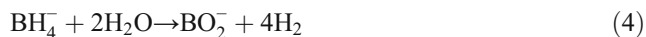
It is important to develop the best composition of the anode material in order to improve the efficiency of oxidation

✉ Grzegorz Lota
Grzegorz.Lota@put.poznan.pl

¹ Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland

² Institute of Non-Ferrous Metals Division in Poznan Central Laboratory of Batteries and Cells, Forteczna 12, 61-362 Poznan, Poland

reaction. The actual number of released electrons is generally fewer than the theoretical (i.e. $8 e^-$) because of the parallel reaction of hydrolysis which can take place [5, 6]:



The most commonly used catalyst is platinum, but it limits the commercialization of fuel cells due to the high cost. It is possible to utilize less expensive catalysts (Ag, Ni), but they are suppressed by alkaline medium [7]. In order to increase the surface area of anode material, cheap conductive carbon supports are used [8, 9].

Multicomponent hydrogen storage alloys such as AB_5 and AB_2 types are usually used as the negative materials in nickel-metal hydride (Ni-MH) batteries. The alloys are a special group of anode materials also employed in direct borohydride fuel cells, because they can absorb atomic hydrogen associated with a decreased evolution of the gas and can be used instead of the noble metals [10, 11]. Moreover, rare earth metal-based AB_5 -type alloys have a high catalytic activity relative to electrochemical oxidation of hydrogen. Good results are obtained using Ni-based composite catalysts smeared onto a nickel foam [12]. Ni-based materials provide the most negative potential, compared to usually used electrode materials, but less than $8 e^-$ is involved in process of oxidation of borohydride, probably due to hydrolysis at the anode surface [5]. Adding silicon to hydrogen storage alloys causes the borohydride hydrolysis reaction to inhibit because of poor catalytic activity [13]. Better electrochemical properties of anode for DBFC were also obtained for composite electrodes with carbon materials [14].

Therefore, in this paper, the electrochemical performance of the oxidation reaction was evaluated by comparing anode material modified using graphite, silicon or carbon nanotubes.

Materials and methods

In order to prepare the working electrode, the commercial AB_5 -type alloy (TREIBACHER) of formula $\text{LaMnNi}_{3.55}\text{Al}_{0.30}\text{Mn}_{0.40}\text{Co}_{0.75}$ was used. This alloy is described by the following composition: Mm = La-rich mischmetal 33.1 wt.%, La 53.3 wt.%, Ce 33.7 wt.%, Nd 9.8 wt.%, Pr 3.2 wt.% and other rare earth metals 66.9 wt.%, Ni 47.8 wt.%, Co 10.12 wt.%, Mn 5.10 wt.%, and Al 1.86 wt.%. The alloy was mixed with nickel carbonyl (30 wt.%) and carbon nanotubes (ALDRICH CHEMISTRY) or graphite (Lonza) or silicon powder (ALDRICH CHEMISTRY) in an amount of 3 wt.%. To ensure the homogeneity of the electrode material, ball milling was applied for 6 min. For this purpose, a ball mill (SPEX Sample Prep Q Mixer/Mill 8000 M) was used. Then, the composite material was blended with a 3 wt.% poly(vinyl alcohol) solution as a

binder. This resulting mixture (250 mg) was coated into a 1 cm x 1 cm nickel foam (porosity >95%); therefore, the catalyst loading equals ca. 250 mg cm^{-2} . The next step was to dry electrodes for 24 h at 50 °C, and then the pasted electrodes were pressed under a pressure of 10 MPa. A scanning electron microscope (SEM EVO[®]40 ZEISS) was used to analyse the structures of the additives and anode materials.

A three-electrode measurement system was built of the working electrode, the counter electrode made of the nickel foam and the Hg/HgO electrode as the reference one, immersed in 60 ml of fuel solution. For the sake of the paper, the electrochemical tests were examined using 6 M NaOH and 6 M KOH containing 0.5 M NaBH_4 (ALDRICH CHEMISTRY) as a fuel. Before testing, the electrode was chemically activated by being immersed in 6 M KOH or 6 M NaOH solution for 24 h. Electrolyte conductivities were estimated using the conductometer CPC-505 (Elmetron). The electrochemical measurements were carried out using cyclic voltammetry (the scanning rate was 5 mV s^{-1} , potential ranged from 0 to 1.15 V vs. Hg/HgO electrode), chronopotentiometric measurements with the constant current density of 100 mA g^{-1} , calculated on active mass of electrode and electrochemical impedance spectroscopy.

The electrical conductivity (at room temperature) was examined by impedance spectroscopy at the frequency 1 kHz. Conductivities of active masses were estimated after applying ball milling process. Samples were placed in a hollow cylinder with the inner diameter 1.494 cm. Each of them was compressed in air between two steel pistons under the pressure 40 MPa. The value of resistance was estimated at frequency 1 kHz and the electrical conductivity is given by Eq. (5):

$$\sigma = \frac{l}{R \cdot A} \quad (5)$$

where R is a resistance (Ω), A is an area of the piston surface (cm^2), l is a height of the sample (cm) and σ is an electrical conductivity (S cm^{-1}). All electrochemical data were carried out using the potentiostat/galvanostat VMP3/Z (Biologic, France).

Results and discussion

To obtain the optimum anode composition, three additives (two types of carbon and silicon) were tested. All components of composite materials were mixed using ball milling in order to obtain a homogenous active mass of electrodes. Table 1 presents the properties of composites.

The addition of carbon materials increases the conductivity of the unmodified composite NCAU (Ni: 30 wt.% + Aurestore IV: 70 wt.%), which is the most visible in the case of graphite.

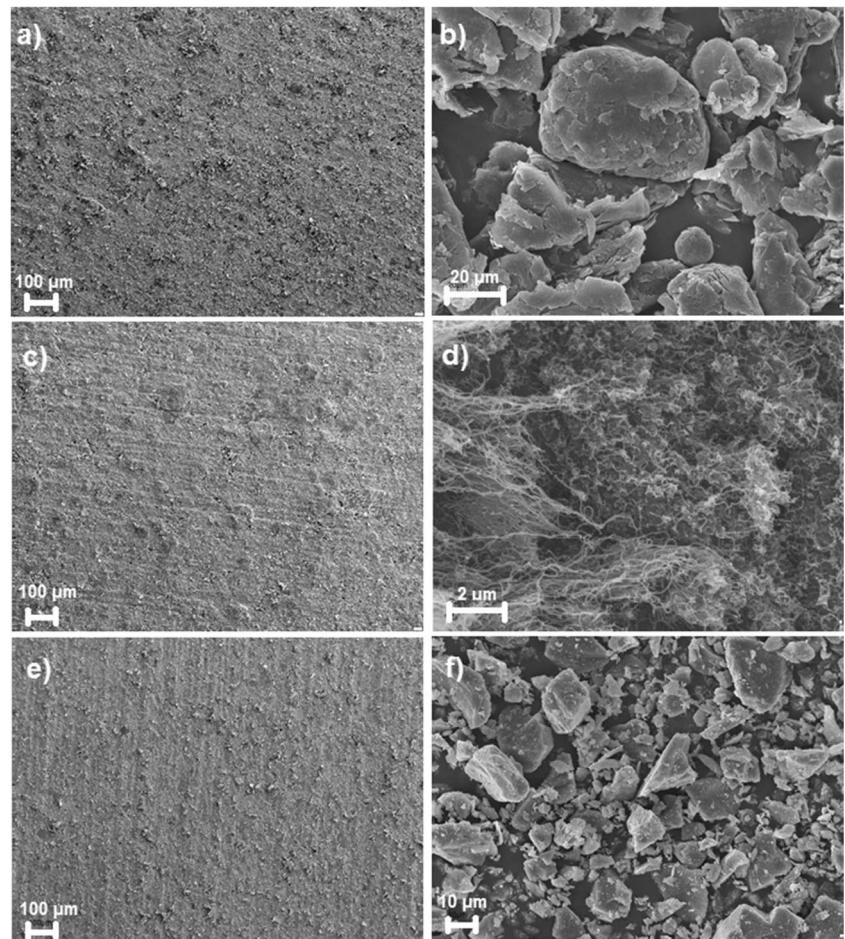
Table 1 Properties of anode compounds with appropriate abbreviations

Sample	Abbreviation	Conductivity S cm ⁻¹
Graphite	G	1.3
Carbon nanotubes	N	1.8
Silicon powder	S	0.071
Nickel carbonyl	NC	11
Aurestore IV	AU	15
Graphite 3 wt.% + Ni 30 wt.% + Aurestore IV 67 wt.%	GNCAU	20
Carbon nanotubes 3 wt.% + Ni 30 wt.% + Aurestore IV 67 wt.%	NNCAU	13
Silicon powder 3 wt.% + Ni 30 wt.% + Aurestore IV 67 wt.%	SNCAU	13

The morphologies of anode materials were evaluated by the scanning electron microscopy. SEM images were performed on carbon materials: graphite flakes, MWNT O.D. 110–170 nm and silicon particles, and electrodes with the additives are shown in Fig. 1. The scaly structure of graphite can be seen in Fig. 1b, d shows the network created by commercial carbon nanotubes and Fig. 1f illustrates fine and irregular grains of silicon. The homogeneity of the electrode active materials is well visible in Fig. 1a, c and e.

To estimate the influence of different additives on the electrochemical performance, in the first step, measurements were carried out for composite material containing 30% of carbonyl nickel and 70% of multicomponent hydrogen storage alloy, which was chosen as reference system, and labelled as unmodified electrode. For that composition of anode for DBFC, the most suitable electrolyte was selected. Figure 2a shows I-E curves for two types of electrolytes. It is well known that DBFC performance strongly depends on the

Fig. 1 SEM images of **a** anode with graphite, **b** the flake graphite, **c** anode with MWNT 110–170 nm, **d** MWNT O.D. 110–170 nm, **e** anode with silicon and **f** silicon particles



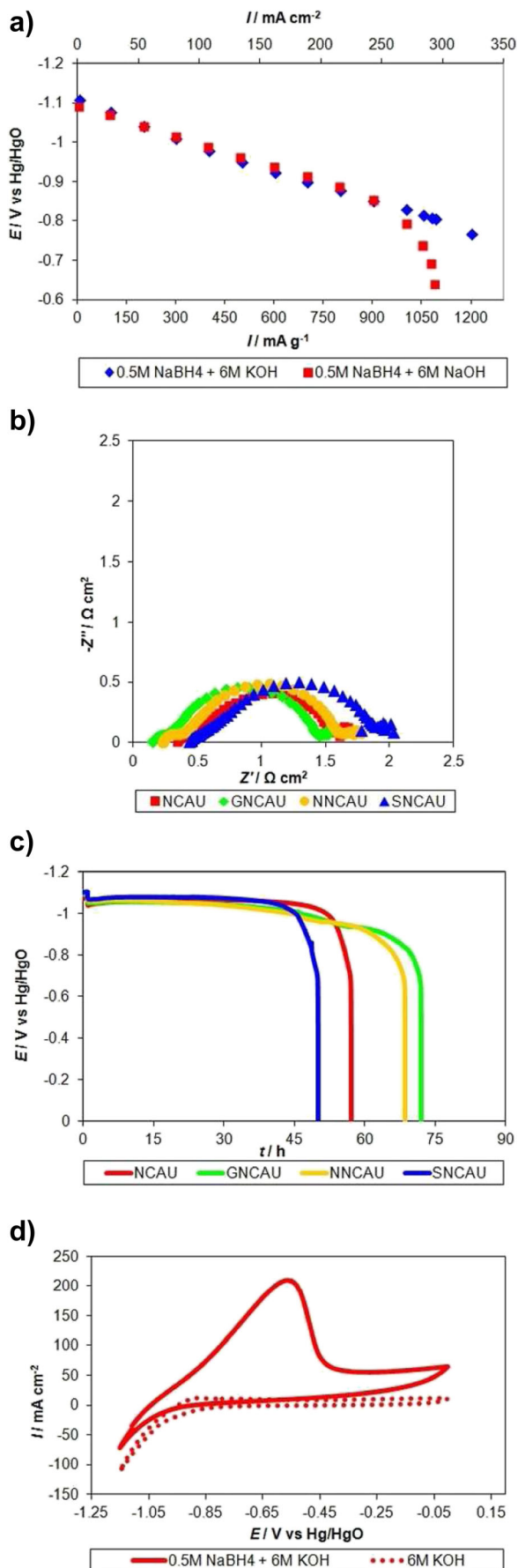


Fig. 2 Electrochemical characteristics. **a** Polarization curves for unmodified anode (30% Ni + 70% Aurestore IV) in different electrolytes. **b** Nyquist plots of composites carried out in 0.5 M NaBH₄/6 M KOH electrolyte. **c** Chronopotentiometry curves of composites (with current density 100 mA g⁻¹) carried out in 0.5 M NaBH₄/6 M KOH electrolyte. **d** Cyclic voltammety characteristics (5 mV s⁻¹) for graphite composites in 0.5 M NaBH₄/6 M KOH and supporting electrolyte 6 M KOH

concentration of fuel and supporting electrolyte. The following types of electrolytes were tested: 0.5 M NaBH₄/6 M NaOH and 0.5 M NaBH₄/6 M KOH. After the working electrode was immersed in 0.5 M NaBH₄ and aqua solution of 6 M NaOH or 6 M KOH, the OCP was around -1.1 V vs. Hg/HgO electrode. When the polarization characteristics are analysed, it can be concluded that the best results were reached in a 0.5 M NaBH₄ + 6 M KOH electrolyte. Sodium borohydride is known as a cheaper hydrogen generator with excellent efficiency of hydrogen storage. Potassium hydroxide has a higher conductivity than sodium hydroxide (617 mS cm⁻¹ for 6 M KOH and 366 mS cm⁻¹ for 6 M NaOH) as a supporting electrolyte. There is the most linear decrease of potential with increasing current density; therefore, this type of electrolyte was selected for further tests.

There is a correlation between the activity of the metal nanoparticles and their size, so carbon materials can be used as catalyst supports in fuel cells thanks to their high surface area and chemical stability [15]. However, adding carbon nanotubes lowered the packing density of alloy particles in three-dimensional porous nickel foam and scarified the structure of pasted electrode during measurements.

Figure 2b shows the Nyquist plots. The impedance spectra consist of the semicircles. All electrode materials are characterized by the various value of ESR (0.148, 0.233, 0.349 and 0.441 Ω for graphite, carbon nanotubes, unmodified and silicon electrode, respectively, in 0.5 M NaBH₄/6 M KOH). The composite modified with 3% of silicon exhibits the highest equivalent series resistance, which is related to the lowest conductivity value of pure silicon powder (Table 1). The diameter of semicircles at low frequencies is attributed to the charge transfer resistance of borohydride oxidation reaction [16, 17]. It should be noted that the composite material containing 3% of carbon nanotubes exhibit slower charge transfer resistance than those using graphite or silicon powder. It means that the reactions take place at quite a high rate, which may indicate an intensive gassing observed after immersing the anode into the borohydride solution.

Probably due to the way electrode material is prepared using a simple ball milling process, the activation is accelerated [18] and better electrochemical characteristics are obtained. Milling for a short period of time prevents the crystalline structure of hydrogen absorbing alloy from being destroyed.

Another very important aspect of controlling the parameters of fuel cells is their stability. Figure 2c presents the

chronopotentiometric curves of all composites under current load of 100 mA g⁻¹, calculated on active mass of anodes. The experiment showed that the half-cell DBFC maintains stability over 72 h. Graphite as an addition again proved to be better than carbon nanotubes and silicon. Such an additive enhances the utilization of borohydride fuel. The electric charge was calculated using Faraday's law:

1. The theoretical electric charge:

$$Q_1 = \frac{z \cdot F}{M} \quad (6)$$

$$Q_1 = 5.6Ahg^{-1}$$

2. The electric charge obtained using the anode with graphite as an addition:

$$Q_2 = I \cdot t \quad (7)$$

$$Q_2 = 1.72Ah$$

$$R \% = \frac{Q_2}{Q_1} \cdot 100 \% \quad (8)$$

$$R\% = \frac{1.53Ahg^{-1}}{5.6Ahg^{-1}} \cdot 100\% = 27\%$$

Graphite as an addition again proved to be better ($R\% = 27\%$) than carbon nanotubes ($R\% = 26\%$) and silicon ($R\% = 19\%$). Such an additive enhances the utilization of borohydride fuel ($R\% = 23\%$ for unmodified electrode). In the case of carbon nanotubes being added to the electrode material, the highest loss of active material from support was observed during electrochemical measurements (the average weight loss was about 20%), because of hydrogen bubbles, which probably formed as a result of hydrolysis of the borohydride -reaction (4). These calculations show how important it is to work further on improving the performance of anode materials.

The electrochemical performance of anode material for BH_4^- oxidation was also characterized by CV tests in order to determine the processes and reactions attributed to the oxidation and hydrolysis of $NaBH_4$. As shown in Fig. 2d, the anodic peak occurred at the potential of about -0.65 V can be connected with an increasing reaction rate and probably due to good catalytic properties of graphite, because of the reaction of charge transfer and desorption of hydrogen from the surface of multicomponent hydrogen storage alloy.

Hydrogen was also generated as the effect of reducing water, when negative values of current and potential were applied [19]:



Conclusions

Two types of electrolytes and compositions of anode material for direct borohydride fuel cell are compared. The greatest stability of polarization potential for the anode consisted of hydrogen storage alloy with nickel carbonyl was obtained for 0.5 M $NaBH_4$ + 6 M KOH electrolyte; therefore, it was chosen for further measurements. Graphite proved to be the best additive to the anode material. This type of carbon material improved the conductivity of anode composites as well as extended stability of DBFC. Adding silicon to composite with hydrogen storage alloy did not improve the half cell, probably due to its poor catalytic activity. In the case of carbon nanotubes, an increase of efficiency is observed due to their properties with the simultaneous highest loss of active material from three-dimensional porous nickel foam. To summarize, the addition of 3% of graphite to composite with AB_5 -storage alloy would be a promising supplement for half cell of DBFC application.

Acknowledgements The authors acknowledge the financial support from the European Fund of Regional Development within the framework of the operating program "Innovative Economy 2007–2013" under Project No. POIG.01.03.01-00-086/09.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Wee JH (2006) Which type of fuel cell is more competitive for portable application: direct methanol fuel cells or direct borohydride fuel cells? *J Power Sources* 161:1–10
2. Ma J, Choudhury NA, Sahai Y (2010) A comprehensive review of direct borohydride fuel cells. *Renew Sustainable Energy Rev* 14: 183–199
3. Choi JP, Seo YH, Kim BH (2011) Stand-alone micro direct borohydride fuel cells using mixture of sodium borohydride and potassium hydroxide. *J Mech Sci Techno* 25:931–935
4. Haijun W, Cheng W, Zhixiang L, Zongqiang M (2010) Influence of operation conditions on direct $NaBH_4/H_2O_2$ fuel cell performance. *Int J Hydrog Energy* 35:2648–2651
5. de Leon CP, Walsh FC, Pletcher D, Browning DJ, Lakeman JB (2006) Direct borohydride fuel cells. *J Power Sources* 155:172–181
6. Celik C, Boyaci San FG, Sarac HI (2008) Effects of operation conditions on direct borohydride fuel cell performance. *J Power Sources* 185:197–201
7. Stoševski I, Krstić J, Milikić J, Šljukić B, Kačarević-Popović Z, Mentus S, Miljanić Š (2016) Radiolitically synthesized nano Ag/C catalysts for oxygen reduction and borohydride oxidation reactions in alkaline media, for potential applications in fuel cells. *Energy* 101:79–90

8. Duan D, Liu H, You X, Wei H, Liu S (2015) Anodic behavior of carbon supported Cu@Ag core-shell nanocatalysts in direct borohydride fuel cells. *J Power Sources* 293:292–300
9. Behmenyar G, Akin AN (2014) Investigation of carbon supported Pd-Cu nanoparticles as anode catalysts for direct borohydride fuel cell. *J Power Sources* 249:239–246
10. Liu BH, Suda S (2008) Hydrogen storage alloys as the anode materials of the direct borohydride fuel cell. *J Alloys Compd* 454:280–285
11. Wang L, Ma C, Sun Y, Suda S (2005) AB₅-type hydrogen storage alloy used as anodic materials in borohydride fuel cell. *J Alloys Compd* 391:318–322
12. Ma J, Sahai Y, Buchheit RG (2010) Direct borohydride fuel cell using Ni-based composite anodes. *J Power Sources* 195:4709–4713
13. Wang L, Ma C, Mao X (2005) LmNi_{4.78}Mn_{0.22} alloy modified with Si used as anodic materials in borohydride fuel cells. *J Alloys Compd* 397:313–316
14. Lota G, Sierczynska A, Acznik I, Lota K (2014) AB₅-type hydrogen storage alloy modified with carbon used as anodic materials in borohydride fuel cells. *Int J Electrochem Sci* 9:659–669
15. Antolini E (2009) Carbon supports for low-temperature fuel cell catalysts. *Appl Catal B-Environ* 88:1–24
16. Liu BH, Li ZP, Arai K, Suda S (2005) Performance improvement of a micro borohydride fuel cell operating at ambient conditions. *Electrochim Acta* 50:3719–3725
17. Qin H, Liu Z, Lao S, Zhu J, Li Z (2010) Influences of carbon support on the electrocatalysis of polypyrrole-modified cobalt hydroxide in the direct borohydride fuel cell. *J Power Sources* 195:3124–3129
18. Li X, Wang L, Dong H, Song Y, Shang H (2012) Electrochemical hydrogen absorbing properties of graphite/AB₅ alloy composite electrode. *J Alloys Compd* 510:114–118
19. Wang L, Ma C-A, Mao X, Sheng J, Bai F, Tang F (2005) Rare earth hydrogen storage alloy used in borohydride fuel cells. *Electrochem Commun* 7:1477–1481