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Promotion of the electrochemical hydrogenation of nitrobenzene at hydrogen storage alloys studied using a solid electrolyte method

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Abstract

The electrocatalytic properties of an AB_5-type hydrogen storage alloy towards the electrochemical hydrogenation of unsaturated organic compounds have been studied by a solid electrolyte method using electrochemical hydrogenation of nitrobenzene as a model reaction. Voltammetric studies reveal that the kinetics of the nitrobenzene electro-reduction on the hydrogen storage alloy electrode is similar to that on a Ni electrode. Aniline and *p*-aminophenol are produced as the reaction products. Compared to the Ni electrode, the production of aniline is considerably promoted on the hydrogen storage alloy electrode. Modifying the alloy surface with a thin layer of Cu enhances the reaction selectivity and current efficiency for aniline formation. Compared to a Cu electrode, the electrochemical hydrogenation of nitrobenzene to aniline is promoted on the Cu-modified alloy electrode. The hydrogenation promotion effect is attributed to the chemical reaction between nitrobenzene and metal hydrides that are electrochemically generated *in situ*. Hydrogen storage alloys therefore make it possible to intensify the electrochemical hydrogenation process of unsaturated organic compounds.

1. Introduction

Hydrogenation is one of the most important reactions used in chemical synthesis. A great number of organic and inorganic compounds having various unsaturated functional groups have been hydrogenated via chemical or electrochemical approaches. Noble metals are the most frequently used catalysts for heterogeneous catalytic hydrogenation reactions [1]. Hydrogen storage intermediate compounds have recently been studied as liquid-phase hydrogenation catalysts because of their higher specific activity than those of the traditional industrial catalysts [2, 3]. High product selectivity, decreased reaction temperature and improved catalyst stability have been demonstrated. Thus, the application of the hydrogen storage intermetallic compounds makes it possible to intensify the processes of industrial liquid-phase hydrogenations.

Compared to the chemical hydrogenation processes, the electrochemical route can generate the hydrides *in situ* and control the activity of mobile active hydrogen. Moreover, the hydride generation process can be reversed. The synthesis of highly pure product with a good yield can be achieved via this route [4]. In this work, an AB_5-type intermetallic compound has been studied as a catalyst for the electrochemical hydrogenation of nitrobenzene using a solid polymer electrolyte method. The most important advantage of this method is that the supporting electrolyte encountered with traditional electrosynthesis can be avoided and the electron-exchange reaction is confined at the interface between the solid electrolyte and the catalysts [5, 6]. The reaction occurring at the catalyst surfaces away from the interface is likely to be distinguished.

2. Experimental details

2.1. *Chemical reagents and instruments*

Nitrobenzene (NB), aniline (AN), *p*-aminophenol (*p*-AP) and methanol were of analytic grade and were used without further purification. The AB_5-type hydrogen-storage alloy used was $Mm(NiCoMnAl)_5$ alloy powder with a particle size of 100~200 mesh. The Mm stands for misch-metal, which is a mixture of rare-earth metals, mainly cerium. The alloy powder was coated with copper by mixing the alloy powder with hydrated $CuSO_4$. The original and Cu-coated alloys are denoted as MH and Cu–MH in the following sections. For the purpose of comparison, electrolytic nickel and copper powders with particle size from 200 to 400 mesh were used.

Cyclic voltammograms were measured with an AFRDE 5 Potentiostat (Pine Company) and an *X–Y* recorder. Current-controlled preparative electrolysis was carried out with a galvanostat apparatus made in our laboratory.

2.2. *Preparation of membrane–electrode-assembly (MEA)*

Nafion® 117 membrane was used as the solid polymer electrolyte material, and platinum was deposited on one side of the membrane by an electroless plating method [7]. The platinized Nafion membrane was rinsed and stored in doubly distilled water. The working electrodes were prepared by the following procedure. The mixture of 80 wt% metallic powder and 20 wt% Teflon binder was packed into a foam nickel substrate with a thickness of 2 mm. The resulting electrodes were dried and then pressed to 0.25 mm in thickness. The MEA was constructed by pressing the working electrode thin film against the platinum-free side of the membrane. During operation the platinum counter electrode was exposed to doubly distilled water and the working electrodes were exposed to organic phase.

2.3. *Electrochemical cells and electrolysis*

The details of an all-solid electrochemical cell used for electrochemical measurements were described in our previous work [8]. The preparative electrolytic cell was composed of two main compartments that were separated by the MEA, Figure 1. The effective geometric surface area of the electrolysis electrode was 3.14 cm^2. The cathode compartment was filled with 5 ml 0.91 mol dm^{-3} (10 V%) NB in methanol, and the anode compartment was filled with doubly distilled water. The total charge passed during each run was 360 C.

2.4. *Product analysis*

Product mixtures were analyzed using a LC-10 liquid chromatography (Japan Analytic Industry), which was fitted with a C-18 column of 15 cm in length. The wavelength of the UV-Vis detector (Soma) was fixed at 290 nm. The column temperature was about 35 °C. The mixture of 50 V% methanol, 20 V% acetic ether and 30 V% water was used as the eluent. The flow rate of the eluent was about 0.8 ml min^{-1}. Under these conditions, the retention time for NB, AN and *p*-AP was 2.9, 3.7 and 5.3 min, respectively. After electrolysis, the mixture was diluted using methanol and was then analyzed without further treatment. The amounts were determined quantitatively from HPLC calibrated with authentic samples.

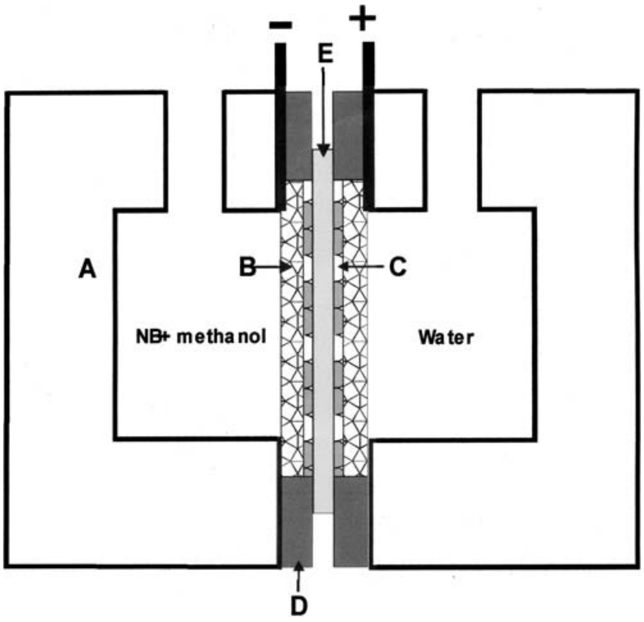

Fig. 1. Schematic diagram of a preparative electrolysis cell. (A) PTFE cell body, (B) Porous platinized titanium supporter, (C) Porous catalyst layer, (D) Silicon rubber gasket, (E) Nafion® 117 membrane.

3. Results and discussion

3.1. *Voltammetric measurements*

Cyclic voltammograms of the powdery electrodes on the Nafion® membrane were measured in the presence of 0.29 mol dm^{-3} (3 V%) nitrobenzene in methanol at a scan rate of 100 mV s^{-1}. Their corresponding base voltammograms were measured at the same scan rate using nitrogen gas through the working electrode compartment. The cyclic voltammograms of MH and Ni show similar properties, as shown in Figure 2 (a) and (b), respectively. The electrochemical reduction of nitrobenzene commences at around 0.40 V (vs. Ag/AgCl, the same below) and broad current waves are seen during the negatively-going scans. After correcting the base responses, the peak potentials can be defined at 0.705 and 0.710 V for the MH and Ni electrodes, respectively. Because the potential is scanned from 0.05 V where no reaction occurs, the increase in base current values with increasing overpotential shown in dotted lines should be caused by the hydrogen evolution reaction. In the presence of the NB–methanol solution, we believe the hydrogen evolution reaction is responsible for the current value increase over the broad current waves since the electrochemical reduction of methanol does not occur in the potential range applied [9]. The voltammetric parameters are listed in Table 1.

Cyclic voltammograms of powdery Cu-modified MH and Cu electrodes on the Nafion membrane surface in the presence of 0.29 mol $^{-3}$ (3 V%) nitrobenzene–methanol solution are shown in Figure 3 (a) and (b). The voltammetric properties are similar with

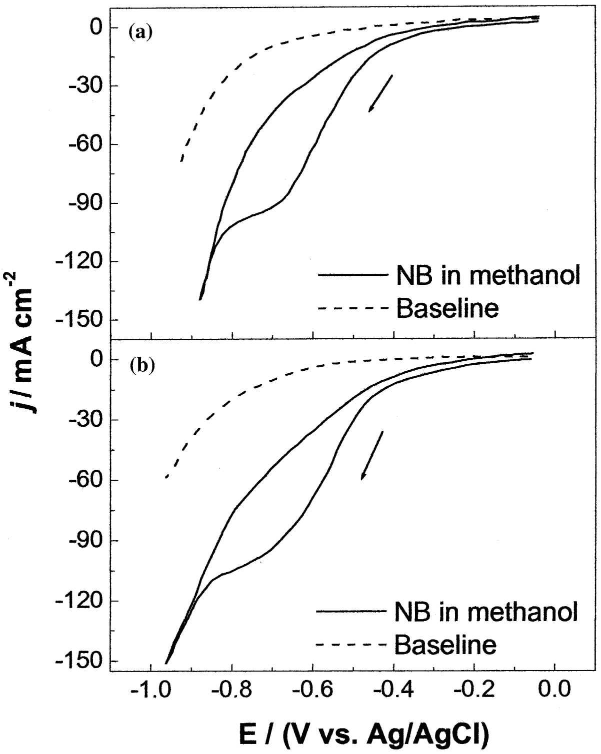

Fig. 2. Cyclic voltammograms for powdery hydrogen storage alloy (a) and Ni (b) on Nafion membrane surface in the presence of 0.29 mol dm^{-3} nitrobenzene – methanol solution (Solid line), and corresponding base voltammograms recorded in the absence of the organic phase (dash line) (dE/dt: 100 mV s^{-1}).

well-defined peaks seen at around 0.625 V. The onset potentials of considerable nitrobenzene reduction are about 0.40 V. Other voltammetric parameters are collected in Table 1.

Extensive investigations of the electrochemical reduction of nitrobenzene on Cu electrodes in aqueous acidic solutions [10, 11] and polymer electrolytes [12–14] have suggested that the nitrobenzene reduction is a totally irreversible reaction under diffusion control. Cyclic voltammograms for the nitrobenzene reduction are characterized by a single cathodic current peak proportional to the square root of scan rate during the negative-going scan and no any peak is observed during the reverse scan. Growing current over the cathodic peak has been suggested to be caused by the hydrogen evolution reaction. Our results are obviously consistent with the literature data. It is therefore reasonable that the cathodic current peaks and the following current growth at more negative potentials result from the transport limitation and the considerable hydrogen evolution reaction respectively, for the nitrobenzene reduction at the interfaces between the powdery electrodes and the Nafion® membrane.

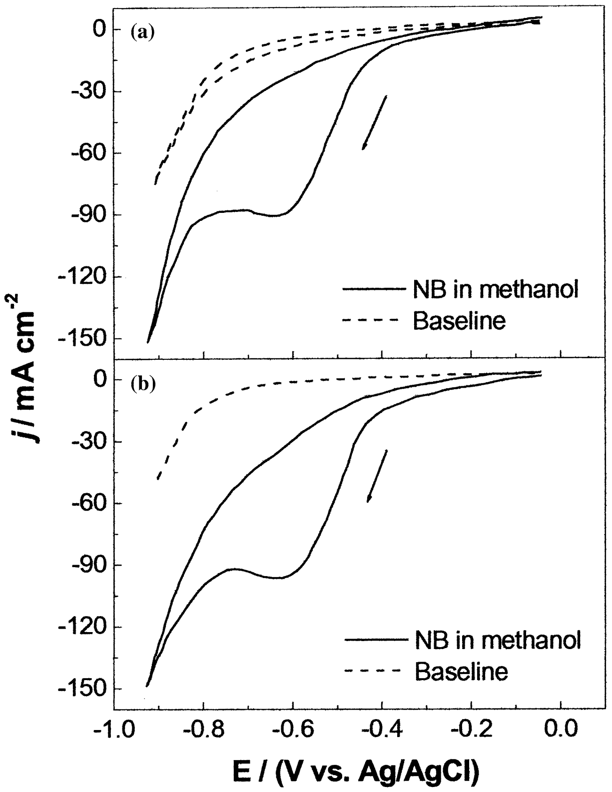

Fig. 3. Cyclic voltammograms for powdery Cu-modified hydrogen storage alloy (a) and Cu (b) on Nafion membrane surface in the presence of 0.29 mol dm^{-3} nitrobenzene–methanol solution (Solid line), and corresponding base voltammograms recorded in the absence of the organic phase (dash line) (dE/dt: 100 mV s^{-1}).

For a totally irreversible electrochemical reaction, the peak potential (E_p) is written as [15]:

$$E_p = E^\circ - \frac{RT}{\alpha n_\alpha F}\left[0.780 + \ln\left(\frac{D^{1/2}}{k^\circ}\right) + \ln\left(\frac{\alpha n_\alpha F v}{RT}\right)\right] \tag{1}$$

where E° is the standard electrode potential, k° is a standard rate constant and other terms have their normal meanings. The term $\alpha\ n_\alpha$ is given by:

$$\left|E_p - E_{p/2}\right| = \frac{48}{\alpha n_\alpha}\text{mV} \tag{2}$$

where $E_{p/2}$ is the potential at half peak height. The value of k° cannot be calculated since E° is unavailable under our conditions. However, E_p can still be used as an

Table 1. Voltammetric parameters (E_p: peak potential; $E_{p/2}$: potential at half-peak height; j_p: peak current density) for 0.29 mol dm^{-3} nitrobenzene in methanol at the interfaces between powdery electrodes and Nafion 117 membrane at 100 mV s^{-1}

Electrode	E_p/V	$E_{p/2}$/V	$\lvert E_p - E_{p/2}\rvert$/V	$\lvert j_p\rvert$/mA cm^{-2}	$\alpha\ n_\alpha$
MH	−0.705	−0.573	0.132	81	0.36
Ni	−0.710	−0.568	0.143	86	0.34
Cu–MH	−0.625	−0.513	0.112	80	0.43
Cu	−0.625	−0.505	0.120	93	0.40

electcrocatalytic parameter. If other terms remain constant in Equation (1), the increase of k° would lead to the positive shift of E_p. The value of k° can be compared from the difference of E_p according to the following formula derived from Equation (1) if other terms are assumed the same:

$$E_{\text{p},2} - E_{\text{p},1} = \frac{\text{RT}}{\alpha n_\alpha F}\ln\left(\frac{k_2^\text{o}}{k_1^\text{o}}\right) \qquad (3)$$

Based on $E_\text{p} - E_{\text{p}/2}$ values in Table 1 and Equation (2), αn_α values are very close for the nitrobenzene reduction reaction on MH and Ni electrode. Similarly, the closeness in the αn_α value is observed on Cu–MH and Cu electrodes. Based on Equation (3), the electrocatalytic activities of MH, Ni, Cu–MH and Cu can be compared. The rate constant of the nitrobenzene electro-reduction reaction on the MH electrode is very close to that on the Ni electrode. The modification of the MH with a thin Cu layer can considerably improve the electrode activity until the activity is close to that of the Cu electrode. These results can be explained by the electrode surface sensitivity of the nitrobenzene reduction [16]. After the MH electrode is coated by the thin layer of Cu, the electron exchange reaction occurs exclusively at the Cu-modified layer. The Cu–MH electrode is expected to become as active as the Cu electrode for the nitrobenzene reduction reaction.

3.2. *Preparative electrolysis*

LC analyses of diluted cathodic mixture after a constant charge show aniline, *p*-AP and unreacted nitrobenzene. The percentage current efficiency (η) was calculated from the change in the concentration of aniline and *p*-AP according to the following equation:

$$\eta = \frac{nFV\Delta c}{Q} \qquad (4)$$

where Q is the total charge passed, V is the volume of the cathodic mixture, Δc is the concentration change before and after an electrolysis and n is the number of electrons transferred per mole of products ($n = 4$ and 6 for AN and *p*-AP, respectively).

Figure 4 shows the variation of current efficiencies for AN and *p*-AP formation as a function of current density at the Ni and unmodified MH electrodes. On the Ni electrode, there is no considerable difference between the current efficiencies for AN and *p*-AP. Such results are similar to literature data obtained for the nitrobenzene reduction at electrodeposited Ni and Nafion membrane interface [17]. On the MH electrode, the current efficiency for *p*-AP has no substantial change. However, a considerable increase of 16% in the current efficiency for the aniline formation has been observed, compared to the Ni electrode. This suggests that the MH electrode can promote the electrochemical hydrogenation of nitrobenzene to AN, although the electrode kinetics are similar on the Ni and MH electrodes. The total maximum current efficiency for the organic reaction is around 60%.

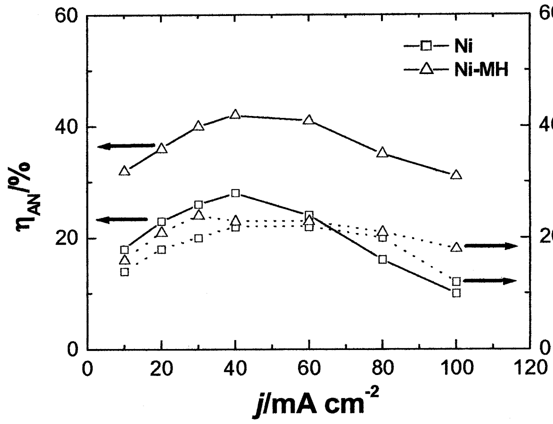

Fig. 4. Current density dependence of current efficiencies for aniline (solid line) and *p*-AP (dotted line) formation on a porous hydrogen storage alloy and Ni electrode.

To improve the selectivity and current efficiency for AN, Cu modified Pt [18, 19] and carbon supported Cu electrodes [20] have been studied for the electrochemical reduction of nitrobenzene in the literature. Only AN is detected for the product of the reduction reaction and the maximum current efficiency is reported to be close to 100% [19]. Coincidently, the modification of MH with Cu has been widely used in the Ni–MH rechargeable battery for improved electrode stability and performance [21, 22]. Figure 5 shows the current density dependence of the current efficiencies for the AN and *p*-AN formation on Cu and Cu–MH electrodes. Compared to the Ni and unmodified MH electrodes, the reduction of NB to AN becomes the main reduction reactions and the formation of *p*-AP is considerably suppressed. The maximum current efficiency for the AN formation is improved to around 61 and 83% on the Cu and Cu–MH electrodes, respectively. In contrast to the literature results obtained on Cu-modified electrodes with AN being the exclusive product, a small amount of *p*-AP is detected in our case. The formation of *p*-AP may

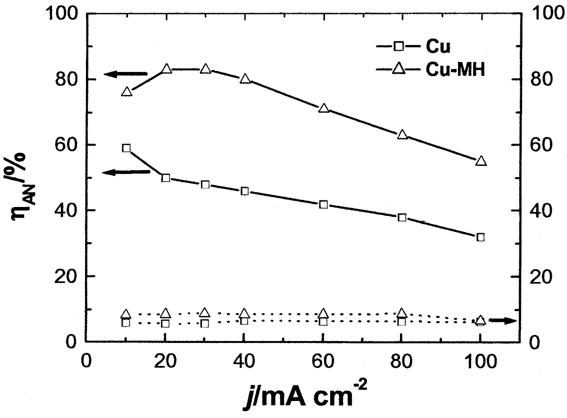

Fig. 5. Variation of current efficiencies for aniline (solid line) and *p*-AP (dotted line) formation on a porous Cu-coated hydrogen storage alloy and Cu electrodes as a function of current density.

be related to the introduction of the foam Ni used as the backbone of the porous electrodes. Compared to the Cu electrode, a promotion of the NB reduction to AN by around 22% at 20 mA cm^{-2} is obtained at the Cu-modified MH electrode.

The decrease in the current efficiency for the AN formation at higher current densities could be attributed to the increased reaction rate of the hydrogen evolution. At high current densities, the hydrogen evolution reaction competes with the electrochemical reduction of nitrobenzene. The concentration polarization caused by the mass transfer of NB would shift the potential negatively. As a result, the rate of the competitive hydrogen evolution reaction is likely to increase. Moreover, the influence of the electro-osmotic mass transfer of water through ion exchange polymer electrolyte membranes on the organic electro-synthesis should be considered [5]. In a solid-state cell using the Nafion® 117 membrane, about two molecules of water are usually transferred together with one proton. In our case, a transfer of about 0.13 g of water from the anode to the cathode chamber is expected after a total charge pass of 360 C. Although the volume of transferred water is only around 2.5% of the catholyte volume, the electro-osmotic water flow in the opposite direction to the diffusion of the nitrobenzene to the reaction zone could hinder reactant transfer to the electrode. This could decrease the current efficiency for the nitrobenzene reduction. If the cathode layer has low porosity, the transferred water may accumulate at the interface between the electrode and the membrane especially at high current densities. The water accumulation is likely to decrease the concentration of nitrobenzene in the reaction regions. Consequently, the rate of the nitrobenzene reduction is inhibited and the hydrogen evolution reaction is promoted. Therefore, a porous and thin cathode electrode layer facilitating the removal of water and the diffusion of nitrobenzene would be required. The choice of suitable solvents would also be important for the nitrobenzene reduction in the solid polymer electrolyte cell.

Our voltammetric studies have shown the similarities of the direct electrochemical reduction of NB on MH and Ni, or the Cu–MH and Cu. It is less likely that the promotion of the NB reduction to AN is caused by the acceleration of the direct electrochemical hydrogenation of nitrobenzene. Active metal hydrides are more likely to be produced on the MH or Cu–MH electrodes during the cathodic process than on Ni or Cu electrodes [3]. The metal hydrides could provide additional reaction sites for the nitrobenzene reduction. The main product for heterogeneous catalytic hydrogenation of nitrobenzene is AN [2, 4]. Therefore, the *in situ* generation of the metal hydrides on the MH or Cu–MH is likely to be responsible for the promotion of the NB hydrogenation obtained in Figures 4 and 5. Therefore, the electrochemical hydrogenation of NB on the MH or Cu–MH electrode may proceed through two reaction pathways as shown in Figure 6. The direct electrochemical hydrogenation is via a successive electro-proton addition. The reaction product is strongly dependent upon the electrode surface and other factors. The indirect electrochemical hydrogenation is via the reaction between NB and the metal hydride intermediates. AN is the main product. The rates of the hydrogen diffusion, the NB-hydride reaction and the combination of the hydrogen atoms to H_2 will affect the promotion effect for the hydrogenation reaction. The combination of the hydrogen atoms to H_2 will decrease the current efficiency if the indirect hydrogenation reaction is slow. The diffusion coefficient of hydrogen in the MH alloy ranges from $10^{-7}\sim10^{-11}$ cm^2 s^{-1} [23, 24], depending on experimental methods and the alloy structures. The adsorbed hydrogen can diffuse much faster at the electrode surface than in the electrode bulk [25]. The surface mobility of the hydrogen atom could increase the reaction sites. Both the alloy surfaces contacting the electrolyte membrane and those surfaces away from the membrane are active for the hydrogenation reaction. Varying operating conditions such as current and potential may change the hydrogen mobility on the MH alloy.

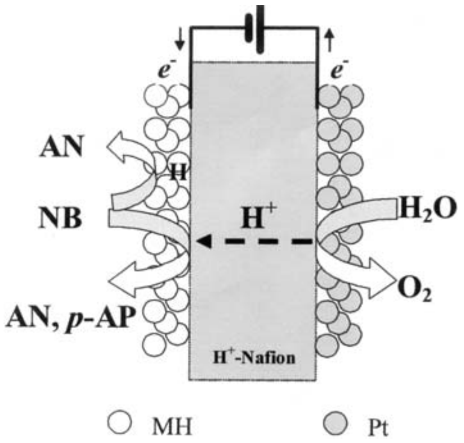

Fig. 6. Scheme of the nitrobenzene electrohydrogenation on porous hydrogen storage electrode in an all solid-state electrolysis cell.

4. Conclusions

The electrochemical hydrogenation of nitrobenzene to aniline through an indirect electrochemical pathway suggests that the hydrogen storage alloy may be an interesting class of electrocatalysts towards the electrochemical hydrogenation of unsaturated organic compounds. The modification of the alloy surface with Cu substantially improves the reaction selectivity for aniline and suppresses the competitive reaction associated with the hydrogen evolution. Combining an all-solid-state electrochemical characterization cell with a preparative electrolysis cell presents a powerful technique for the studies of the organic electrohydrogenation reactions. All solid-state electrochemical reactors for the organic hydrogenation have unique advantages over traditional electrochemical reactors in terms of supporting electrolyte and product purification. Further work should focus on the stability of the modified and unmodified hydrogen storage alloy during the hydrogenation processes.

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