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Hydrogen Generation from Highly Activated Al–Ce Composite Materials in Pure Water

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The reaction of aluminum with pure water is an eco-friendly approach to generate hydrogen. The main difficulty associated with this approach is that an oxide or hydroxide protective film around aluminum particles prohibit the hydrogen generation. In this article, a kind of highly activated Al–Ce composite material has been developed via a convenient ball milling method. Typically, Al–13 wt% Ce has a total hydrogen production of 1134 mL/g and a conversion yield of 92.42% within 60 min. The influences of the cerium concentration and ball milling time on the hydrogen production efficiency are discussed based on XPS, XRD, FESEM, and BET techniques. In addition, the hydrogen production efficiency can be improved by adding alkali chloride (NaCl or KCl) to the Al–Ce composite materials.

I. Introduction

Finding new highly efficient and clean energy sources has become important to researchers due to the increasing energy demand and environmental pollution. Fuel cell is one of the most promising candidates for replacing fossil-fuel power generation. It directly converts chemical energy into electrical energy effectively and avoids environment-pollution problems.[1] Because it has high energy density and only produces environmentally benign water after reacting with air, hydrogen is an ideal fuel for fuel cells. In practical applications, however, hydrogen storage and distribution is a major hurdle for its widespread use due to its relatively low volumetric energy density.[2] Therefore, it is still a great challenge to develop highly efficient direct hydrogen generation materials which can be used in fuel cells and other capable electrical devices.[3,4]

Metal aluminum has been considered as an ideal hydrogen generation material because of its light atomic mass, high electron density, and abundance in the earth's crust. Theoretically, at 25°C and 1 atm, the hydrolysis reaction of 1 g Al can produce 1359 mL of H_2. The generated aluminum oxide hydroxide and/or aluminum hydroxide are eco-friendly and easily recyclable. In addition, aluminum utilization is a user-friendly and safe approach for both hydrogen production and energy storage. However, the reaction of aluminum with pure water is difficult due to a dense oxide film that covers the surface of aluminum.[5] The oxide film is unstable in strong acid or basic solutions. Therefore, it was reported that hydrogen generation took place in basic solutions, which removed the inert Al_2O_3 layer.[5–9] Considering that the use of acid and alkali caused environmental pollution, Deng *et al.* reported that metal Al particle surfaces were modified by fine γ-Al_2O_3 grains.[2,10–15] The dense Al_2O_3 layer was replaced by the loose and porous γ-Al_2O_3 layer, so the inner Al had a chance to react with water. The composition Al-70 wt% γ-Al_2O_3 showed the conversion yield of 88% within 80 h. Alinejad *et al.* reported that aluminum was mechanically milled with fragile salt particles which worked as smaller millers.[16] The salt crystals act to reduce the aluminum particle sizes, damage the dense oxide layer and to form salt gates during the milling process. The milled powder can completely react with pure water at 70°C and quickly release hydrogen within 40 min. Fan *et al.* reported that the hydrogen production is 970 mL/g in 1 *M* NaCl solution from Al–16 wt% Bi alloy after ball milling for 10 h.[17–19] The enhanced hydrogen generation efficiency is explained from the point of micro-galvanic cell between the anode (Al) and cathode (Bi). Kravchenko *et al.* even prepared Al alloy through melting aluminum with a low melting point metal, such as Ga, Bi, Pb, Sn, In and so on.[20] Typically, Al–5.3 wt% Ga–2.0 wt% In–5.4 wt% Sn–7.3 wt% Zn alloy produced hydrogen up to 1000 mL/g in 30 min in pure water. Although metal bismuth, gallium, indium, etc. can activate aluminum, these metals are expensive, toxic, and corrosive. It is practically necessary to find a new kind of environment-friendly metal which can improve the efficiency of hydrogen generation from aluminum. Metal cerium is a good candidate. It is abundant in the earth and has stronger reducibility than Al, so it may damage the dense Al_2O_3 layer more effectively through redox reaction. In addition, the toxicity of neutral CeO_x and $Ce(OH)_x$ is comparable with NaCl, indicating that they are much safer to human beings than basic oxides and hydroxides of alkaline metals and alkaline-earth metals.[21]

In this work, environment-friendly and highly activated Al–Ce composite materials have been prepared by ball milling method. The effects of Ce content and ball milling time on the activity of Al–Ce composites are illustrated in detail. It was thought that the strong reducibility of Ce and unique porous structure of Al–Ce improved hydrogen generation efficiency. In addition, the influence of additives of alkali chlorides on hydrogen production and conversion yield is also discussed.

II. Experimental Procedure

(1) Preparation and Measurements of Al–Ce Composite Materials

Highly pure Al (99.9% purity, 25 μm) and highly pure Ce (99.9% purity, 40 μm) were purchased from Aladdin reagent Co., Ltd. (Shanghai, China) and used without further purification. The mixture of Al and Ce was obtained according to the required weight ratio of Al and Ce. 2.00 g of the mixture and a small amount of pure ethanol was added into a stainless-steel vial and sealed under argon atmosphere. Then ball

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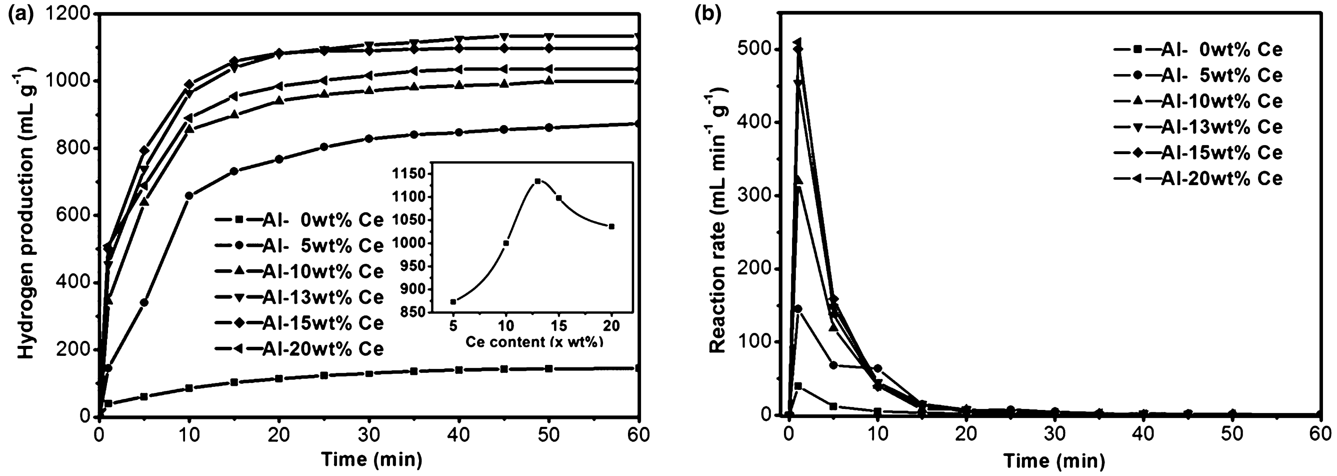

Fig. 1. The hydrogen production curves (a) and the reaction rate curves (b) of 8 h ball-milled Al–*x* wt% Ce composites with pure water.

milling was performed in QM-3SP04 planetary ball miller (made by the Instrument Factory of University of Nanjing) with ball-to-powder mass ratio of 30:1 at a rotational speed of 500 rpm for 1–12 h.

The yield of generated hydrogen was typically measured as follows. Firstly, in the glove box, Al–Ce composites (0.10–0.12 g) were put into a 100 mL Pyrex glass reactor under argon atmosphere. This reactor was placed in a water bath to keep the environment temperature constant at 70°C. Then, 70 mL of distilled water at 70°C was added into the reactor. The hydrogen-generating reaction between Al and water was performed without stirring. After flowing through a condenser, the generated gas was collected in a reverted graduated burette. Its volume can be read directly at any time. Finally, the volume of generated hydrogen was calculated at 1 atm and 25°C. The volume of water vapor was taken into account and removed in the hydrogen yield calculation.

Table I. Hydrogen Generation Rate, Hydrogen Production, Theoretical Hydrogen Production and Conversion Yield at 1 h of Reaction in 70°C Water

	Hydrogen generation rates (mL/min/g)						
Sample	0–5 (min)	5–15 (min)	15–60 (min)	Maximum rate	Hydrogen production (mL/g)	Theoretical hydrogen production† (mL/g)	Conversion yield (%)
Al–0 wt% Ce	12.0	4.3	0.9	39.4	146	1359	10.74
Al–5 wt% Ce	68.0	39.1	3.2	144.8	873	1308	66.74
Al–10 wt% Ce	118.8	24.1	2.1	320.4	1000	1258	79.49
Al–13 wt% Ce	147.8	30.1	2.1	454.3	1134	1227	92.42
Al–15 wt% Ce	158.8	26.5	0.9	500.4	1098	1207	90.97
Al–20 wt% Ce	137.8	26.6	2.0	510.3	1036	1157	89.54

†Calculated assuming that cerium completely reacts with water at 25°C and 1 atm.

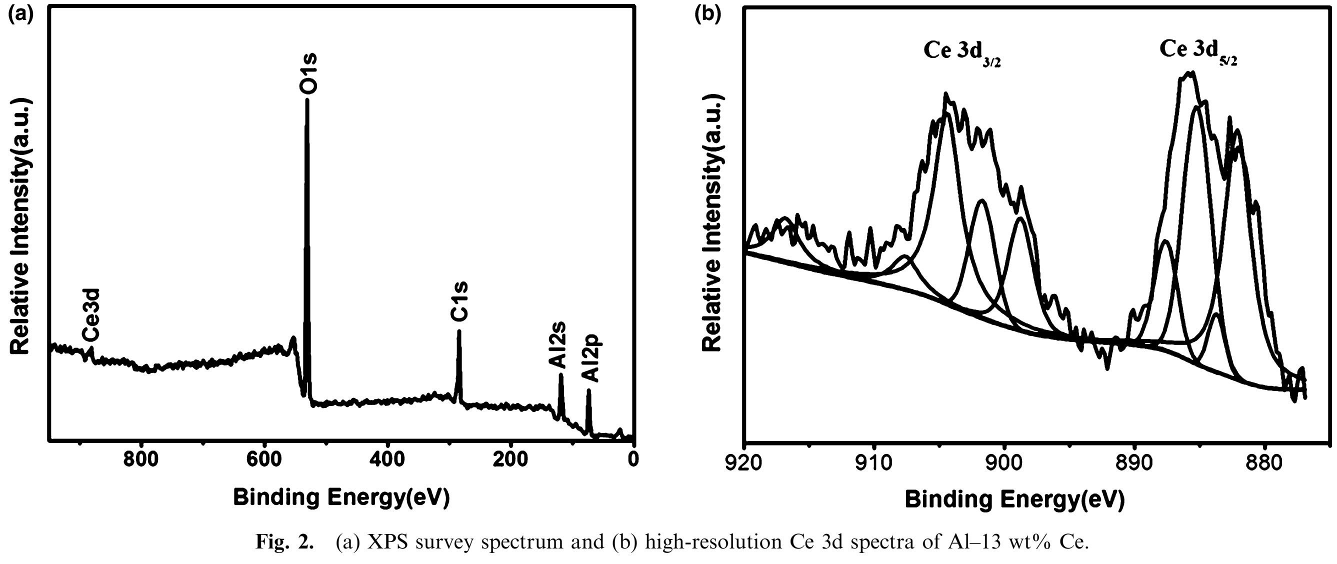

Fig. 2. (a) XPS survey spectrum and (b) high-resolution Ce 3d spectra of Al–13 wt% Ce.

Table II. The Amounts of Different Chemical States Ce in Al–13 wt% Ce

	Chemical states	BE (eV)	Area (%)	Total (at%)
Ce 3d	Ce^0	883.7	2.58	2.58
	Ce^{3+}	885.2	19.62	49.19
		898.8	9.04	
		904.4	20.53	
	Ce^{4+}	882.1	24.81	48.23
		887.6	6.85	
		901.7	8.13	
		907.6	3.63	
		916.8	4.81	

(2) Characterization

The samples were analyzed by X-ray photoelectron spectroscopy (XPS; Perkin-Elmer PHI 5000, Wellesley, MA). All the binding energies were calibrated by using the contaminant carbon (C_{1s} = 284.6 eV) as a reference. The X-ray powder diffraction (XRD) pattern was recorded by using a Japan Regaku (Tokyo, Japan) D/max çA X-ray diffractometer equipped with graphite monochromatized CuKα radiation (λ = 1.5418 Å) irradiated with a scanning rate of 4°/min. The Field-emission scanning electron microscopic (FESEM) images were obtained by using a JEOL (Tokyo, Japan) JSM-7500F microscope operated at an acceleration voltage of 15 kV. The distribution of Ce particles in composite powders was checked by energy dispersive X-ray (EDX) mapping. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area by using adsorption data in the range of the relative pressures ($p/p0$) from 0.02 to 0.20.

III. Results and Discussion

(1) Reactivity of Al–Ce Composite Materials in Water

Hydrogen production, hydrogen generation rate and conversion yield are the most important criteria in evaluating the capability of hydrogen generation materials.[5] Figure 1(a) shows the respective hydrogen production of 8 h ball milled Al–x wt% Ce (x = 0, 5, 10, 13, 15, 20) during 1 h of reaction. All the key parameters about the hydrogen generation property of Al–x wt% Ce series are summarized in Table I. It is found that cerium has a trade-off effect on the hydrogen production. Hydrogen production reaches its maximum at x = 13 and then decreases quickly with the increase of cerium content. The hydrogen generation rate curves of different Al–Ce composites with water are shown in Fig. 1(b). It is obvious that the reaction rate firstly increased and then decreased, and the maximum reaction rate was achieved at 1 min. The increase of Ce content leads to a considerable increase of the reaction rate at 1 min from 39.4 mL/min/g for Al–0 wt% Ce to 510.3 mL/min/g for Al–20 wt% Ce. These data also show that the existence of cerium has made aluminum active.

The positive effect of cerium on the hydrogen-generating reaction is explained in the following two points: Firstly, cerium can damage the dense oxide layer of aluminum during the ball milling process. Reducibility of metal cerium (E^o = −2.336 V) is superior to that of metal aluminum (E^o = −1.662 V), so cerium can damage the dense oxide layer of aluminum through oxidation and reduction reaction, as shown below:

$$Ce + x/3\ Al_2O_3 \rightarrow 2x/3\ Al + CeO_x \qquad (1)$$

It is recently reported that Al–Sn, Al–Bi and Al–Ga–In alloy were prepared through mechanical milling.[17,22] During preparation of these materials, the ball milling plays a main role in ruining the oxide layer. Because their reducibilities are not strong enough, Sn, Bi, and Ga cannot reduce Al_2O_3 layer. By comparison, in our ball milling method, both the reduction of Al_2O_3 by cerium and the mechanical power of ball milling contribute to remove the dense Al_2O_3 layer on the surface of Al particles. Therefore, the as-prepared Al–Ce composites exhibit excellent capability of hydrogen generation as shown in Fig. 1. The XPS investigation of Al–13 wt % Ce was performed for evaluation of their composition. Figure 2(a) is a typical XPS survey spectrum of different atoms. Elements of Al, O, Ce, and carbon contaminant were detected obviously. To clearly reveal the chemical states of

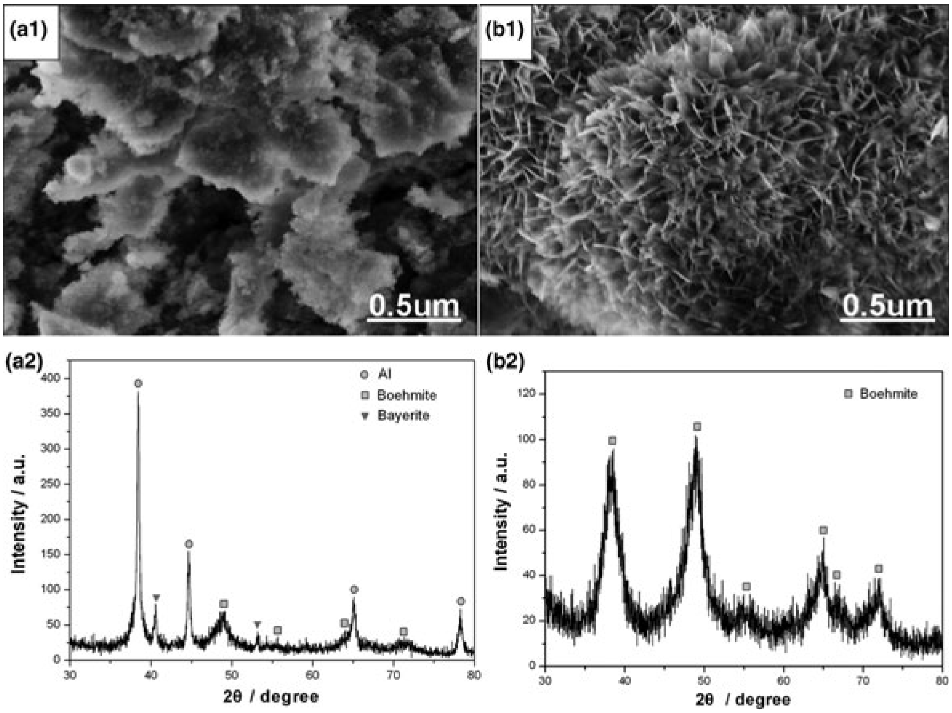

Fig. 3. FESEM micrographs and XRD patterns of the hydrolysis products from 8 h ball-milled (a) Al and (b) Al–13 wt% Ce composite.

the Ce species in Al–13 wt% Ce, Ce 3d spectra are shown in Fig. 2(b). The amounts of Ce were calculated from peaks for Ce^{4+} ions (916.8, 907.6, 901.7, 887.6, and 882.1 eV), peaks for Ce^{3+} ions (904.4, 898.8, and 885.2 eV) and peaks for Ce^0 (883.7 eV). Table II shows that the content of Ce^0 was only 2.58 at%.

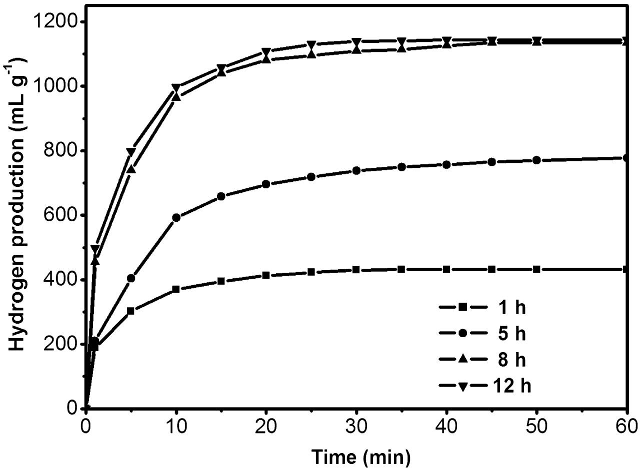

Fig. 4. The hydrogen production curves of Al–13 wt% Ce after different ball-milling times.

Table III. Hydrogen Production and Conversion Yield of Al–13 wt% Ce with 70°C Water after Different Ball-Milling Time

Ball milling time (h)	Hydrogen production (mL/g)	Conversion yield (%)
1	431	35.13
5	778	63.41
8	1134	92.42
12	1143	93.15

Secondly, cerium has an important influence on the morphology of the products generated in the reaction of Al–Ce composites with water. Aluminum without the dense oxide layer can react with water instantly to generate hydrogen, but the hydrolysis products cover aluminum particles and inhibit hydrogen generation.[23] In the ball milling process, cerium elements are dispersed around the surface of aluminum particles. When hydrolysis of Al–Ce composites is performed in pure water, Ce may react with water according to the following reaction[24,25]:

$$\mathrm{Ce} + x\,\mathrm{H_2O} \rightarrow \mathrm{Ce(OH)}_x + x/2\,\mathrm{H_2} \qquad (2)$$

The CeO_x and $Ce(OH)_x$ generated in steps (1) and (2) tend to form loose and porous morphology, moreover, the hydrogen generation rate is quick. Therefore, the hydrolysis products fail to enwrap aluminum particles and inner aluminum particles can continue to react with water. Furthermore, the products will grow into porous structure due to their preferred growth direction.[26]

The FESEM micrograph and XRD patterns of products from the hydrogen generation reaction of (a) ball milled Al–0 wt% Ce and (b) Al–13 wt% Ce composites are shown in Fig. 3. It can be seen in Fig. 3(a1) that the hydrolysis products deposited on the aluminum surface to prevent further reaction, result in the incomplete reaction of aluminum with water. Figure 3(b1) shows that products of Al–13 wt% Ce with water have a flowerlike porous structure. Compared with the former, the latter products are fluffier and more porous, making water continuously react with the core of aluminum particles until the conversion achieves 100%. The hydrogen production at 1 h is from 146 mL/g for Al–0 wt% Ce to 1134 mL/g for Al–13 wt% Ce. The XRD pattern of the ball milling aluminum reacted with pure water is shown in Fig. 3(a2). It can be observed that the peaks are in fundamental agreement with aluminum (No.04-0787), boehmite (No.21-1307) and bayerite (No.20-0011) crystal in the JCPDS database. The high intensity of aluminum in the diffraction pattern implied that the majority of aluminum did not react with water. Figure 3(b2) shows the XRD pattern of Al–13 wt% Ce after reacting with pure water, which is in

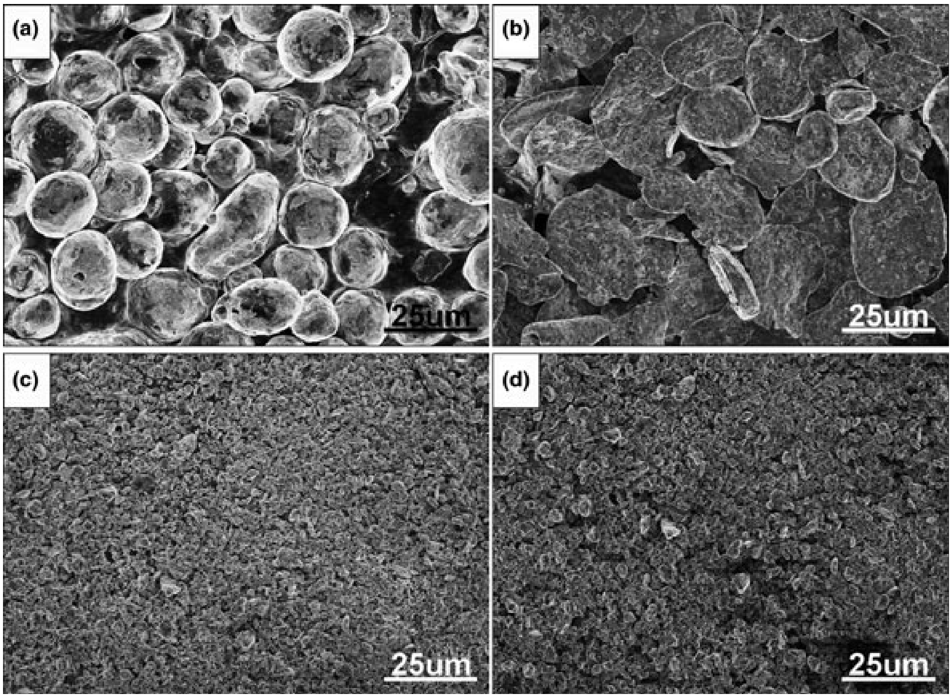

Fig. 5. FESEM micrographs of (a) un-milled Al, Al–13 wt% Ce after ball-milling for (b) 1 h, (c) 8 h, and (d) 12 h.

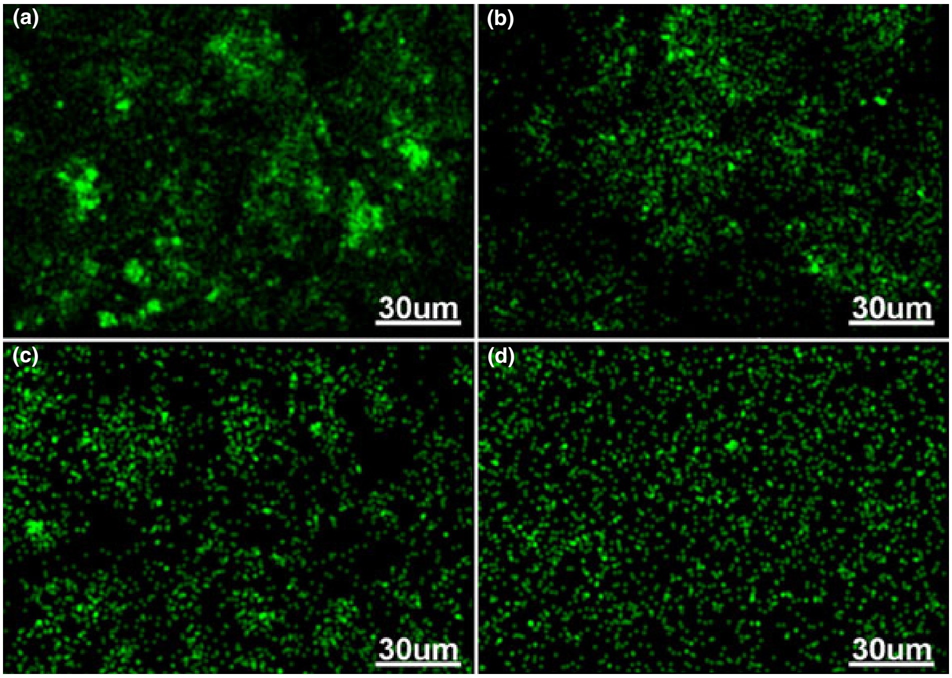

Fig. 6. EDX mapping of Ce in Al–13 wt% Ce composite materials as a function of the milling time: (a) 1 h, (b) 5 h, (c) 8 h, and (d) 10 h.

good agreement with the characteristic peaks of boehmite crystal according to the JCPDS database. Metal aluminum diffraction peaks are incognizable in the diffraction pattern. This implies that reaction has reached the core of aluminum particles, and almost entire aluminum has turned into boehmite.

(2) Effect of Ball Milling Time on the Activity of Al–Ce Composites

Ball milling time is an important parameter in the mechanical alloying process[27] and has a vital impact on the activity of Al–Ce composites. The relationship between hydrogen production and milling time for the ball milled Al–13 wt% Ce composite is shown in Fig. 4. With the increase of milling time, the hydrogen generation rate and the hydrogen production of Al–13 wt% Ce composite increased. It was found that a longer milling time will lead to a higher ability of Al–Ce composites to produce hydrogen when it reacts with water (see Table III).

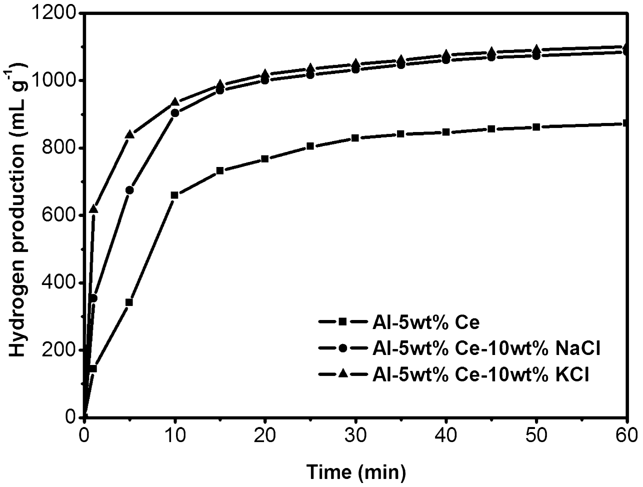

Fig. 7. The hydrogen production curves of 8 h ball-milled Al–5 wt% Ce–10 wt% alkali chloride with pure water.

In the ball milling process, the morphology, microstructure, and composition of metals may change in the repeated flattening, cold welding, and fracturing. It has been proved that the deformed aluminum has a higher activity in water than the strain-free aluminum.[27,28] As shown in Fig. 5, the morphology of the Al–13 wt% Ce composite changed a lot with the increase of milling time. The unmilled aluminum powders were quasi-spheres with diameters of 20–40 μm [see Fig. 5(a)]. When milled for 1 h, the particles of Al–Ce composites are soft, their tendency to flatten, weld together, and form large particles is high [see Fig. 5(b)]. With continued deformation, the particles get work hardened and fracture by the fragmentation of fragile flakes. Fragments generated by this mechanism may continue to reduce in size in the absence of strong agglomerating forces. When milled for 8 or 12 h, the particles of Al–Ce composites became smaller irregular nuggets [see Figs. 5(c) and 4(d)]. Compared with unmilled Al particles, the long-time milled Al–13 wt% Ce composite particles had smaller sizes (~2.5 μm in diameter) and larger specific surfaces. Meanwhile, ball milling induced pitting corrosion process by creating numerous defects and fresh surfaces on metals.[17] All these changes are believed to accelerate and promote the reaction of aluminum with water. Besides particle size and microstructures, the long-time milling also affects the spatial elemental distribution of the

Table IV. Hydrogen Production, Theoretical Hydrogen Production and Conversion Yield at 1 h of Reaction in 70°C Water

Sample	Hydrogen production (mL/g)	Theoretical hydrogen production[†] (mL/g)	Conversion yield (%)
Al–5 wt% Ce	873	1308	66.74
Al–5 wt% Ce–10 wt% NaCl	1085	1173	92.50
Al–5 wt% Ce–10 wt% KCl	1101	1173	93.86

[†] Calculated assuming that cerium completely reacts with water at 25°C and 1 atm.

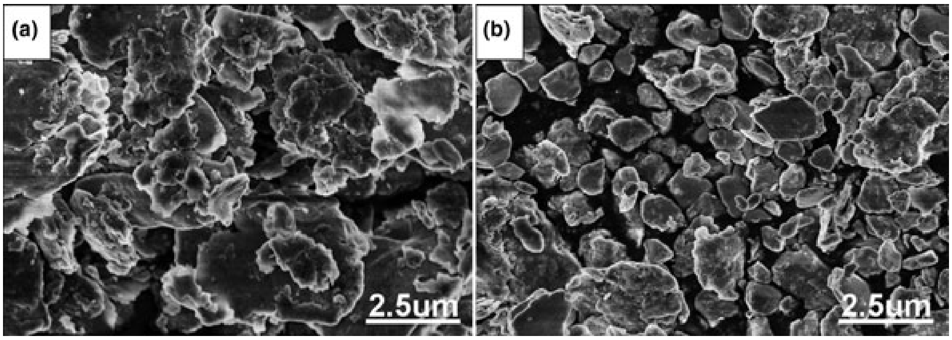

Fig. 8. FESEM micrographs of 8 h ball-milled (a) Al–5 wt% Ce and (b) Al–5 wt% Ce–10 wt% NaCl.

Al–Ce composites. Figure 6 shows EDX mapping of Ce in Al–13 wt% Ce composite materials as a function of the milling time. The cerium particles are distributed unequally when milled for 1 or 5 h. However, when the milling time was prolonged to 8 or 12 h, the particle size of cerium significantly decreased and they are distributed equally around aluminum particles. Based on the previous discussion, Ce plays an important role in destroying the inert Al_2O_3 film and building porous structures of the hydrolysis products. It is reasonably believed that the improved dispersion of Ce in the Al–Ce composites is responsible for the enhanced hydrogen generation effects which depend on the milling time, as shown in Fig. 4 and Table III.

(3) Effect of Alkali Chloride on the Activity of Al–Ce Composites

Figure 7 shows that the alkali chloride (NaCl and KCl) has an important role in the reaction of 8 h ball milled composites with water. Within 60 min, the hydrogen productions are 873, 1085, and 1101 mL/g for Al–5 wt% Ce, Al–5 wt% Ce–10 wt% NaCl and Al–5 wt% Ce–10 wt% KCl, respectively (see Table IV). The addition of alkali chloride obviously improves hydrogen production and reaction rate of the composites. Alkali chloride can help reduce the size and disperse cerium in the Al–Ce composites during the milling process. Since they have sharp edges, alkali chloride particles can reduce the size of aluminum particles. Decreasing size of aluminum particles leads to a rise in kinetics of hydrolysis reaction. As shown in Fig. 8, Al–5 wt % Ce–10 wt% NaCl has a decreased particle size. In a long time ball milling process, NaCl as nano-miller can cause the aluminum particles to reach smaller sizes. The specific surface area increases from 24.3 m^2/g for Al–5 wt% Ce to 30.4 m^2/g for Al–5 wt% Ce–10 wt% NaCl. Moreover, chloride ion can penetrate the aluminum oxide layer and promote the reaction of the composites with water.[29,30] When the composites continuously react with water to cause more corrosion pits, micro hydrogen bubbles gradually form under the aluminum oxide layer. These micro hydrogen bubbles can break down the aluminum oxide layer, resulting in the continuous reaction of aluminum with water. On the other hand, chloride ions can replace the hydroxyl ions, reducing the reaction products deposited on the surface of the composites which always inhibit aluminum from meeting with water.[31]

IV. Conclusions

A new kind of environment-friendly hydrogen generation materials, Al–Ce composites, have been prepared through the high energy ball milling method. The effect of cerium on the activity of Al–Ce composites was studied in detail. The addition of cerium can effectively damage the dense oxide layer and lead to the formation of flower-like nano-flake reaction products. The flowerlike nano-flake structure prevents the products from depositing densely on the surface of composites, so that the composites can continuously react with water. After reacting with water at 70°C for 60 min, the 8 h milled Al–13 wt% Ce composite produces 1134 mL/g hydrogen and the conversion yield reaches up to 92.42%. Furthermore, the effects of ball milling time and alkali chlorides on generating hydrogen were also investigated. Long-time ball milling and the addition of alkali chlorides can increase the dispersity of Ce and decrease the particle size of Al–Ce composites to improve the hydrogen generation capability.

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