Carbon nanotubes/aluminum composite as a hydrogen source for PEMFC

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Al matrix composites reinforced with 0–5 vol. % carbon nanotubes (CNTs) were fabricated by spark plasma sintering (SPS) to examine their hydrogen generation properties from the hydrolysis of Al in 10 wt. % NaOH solution at room temperature. The 5 vol. % CNTs/Al composite exhibits a maximum hydrogen generation rate of 120 ml/min g, which is about 6 times higher than that of Al without CNTs due to the synergetic effects of the porous Al matrix, which has a large reaction area and galvanic corrosion between the Al matrix and the CNTs. The hydrogen gas generated from the hydrolysis of the CNTs/Al composite has high purity without any production of undesirable CO. PEMFC produced electricity at 10 A and 0.73 V for 13 min, with hydrogen generated from the hydrolysis of 3.5 g–5 vol. % CNTs/Al composite. The CNTs/Al composite was effectively used as a hydrogen source for PEMFC.

C O R R E S P O N D I N G   A U T H O R

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I N T R O D U C T I O N

On-board hydrogen generation from the hydrolysis of aluminum (Al) is a low-priced method for supplying hydrogen directly to polymer electrolyte membrane fuel cells (PEMFC). In an alkaline solution, the hydrolysis reaction of Al can be expressed by Eq. (1).

\[ \text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}_2 \]  \hspace{1cm} (1)

One of the major drawbacks of Al is its low hydrogen generation rate compared with those of other on-board hydrogen generation materials such as chemical hydride. As expressed in Eq. (1), the hydrogen generation rate is directly proportional to the oxidation rate of Al. So, Al or Al alloys in the form of powders have mainly been used to achieve a good hydrogen generation rate, which is the result of the large reaction area of the powders [1–9]. Although Al powders exhibit high mass activity for the hydrolysis reaction, they are not suitable for practical use due to their explosiveness when exposed to moisture or a small amount of heat. In addition, to store them safely, Al powders require additional complex equipment. In attempts to use Al as an on-board hydrogen generation material, the development of safe Al in bulk form with a rapid hydrogen generation rate has proven to be a
challenge. The highly porous Al matrix composites can be candidates to solve this problem. Carbon nanotubes (CNTs) are a promising reinforcement for the Al matrix composite due to their extraordinary specific strength. The CNTs reinforced Al matrix composites have become very attractive due to their various structural application areas, such as the automobile, aerospace and aircraft industries [10]. It has been reported that an electrochemically noble phase formed in the Al matrix accelerates the hydrolysis reaction rate via a galvanic corrosion effect [18]. Eom reported that the galvanic current of Al that is electrically connected to carbon is 1.5 times higher than that of the Al bulk state. Therefore, the CNTs/Al composite will exhibit an enhanced hydrogen generation rate due to galvanic corrosion between Al and CNT. It was reported that CNT mixed with Sn–27 wt. % Al alloy powder, synthesized using a high temperature and high pressure method, showed beneficial effects on the hydrogen yield compared with that of the alloy without CNT [19]. However the beneficial effects of CNT were relatively small or less than 10%, and were simply explained as resulting from the increase in the reaction area of the composite of Sn–28%Al and CNT without considering the galvanic corrosion effects between CNT and the Sn–Al alloy [19]. CNTs/Al composites have been widely fabricated by powder metallurgy process. These powders can be consolidated using various techniques such as hot rolling, hot extrusion, compaction, sintering, and spark plasma sintering (SPS) [11–15]. SPS processing is a useful method for densifying hard-to-sinter materials such as CNTs [16]. Furthermore, sound interfacial bonding between the matrix and the reinforcements can be achieved by spark plasma sintering [17]. SPS processed Al has a porous structure with large surface area; its porosity can be easily controlled by changing the applied uniaxial stress.

In the present work, to yield the best possible hydrogen generation rate, the effects of CNT content and porous structure on the hydrogen generation rate were examined to optimize the CNTs/Al composite synthesized by SPS. The CNTs/Al composites were prepared by SPS method by consolidating Al powder and the CNT mixture. The surface area was controlled by changing the applied stress during the SPS process. Further, the feasibility of using hydrogen generated from the hydrolysis of CNTs/Al composite to operate a PEMFC was examined using a single PEMFC cell.

Experimental

CNTs/Al mixtures containing various amounts of CNTs (0–5 vol. %) were prepared by the spark plasma sintering (SPS) method (Model 1050, Sumitomo Coal Mining Co. Japan) using Al powder (purity: 99.9%, particle size: 3 μm) and a CNT mixture. The SPS process was performed at 500 °C for 5 min with a heating rate of 100 °C/min. The applied uniaxial stress was changed from 20 to 30, and then to 50 MPa. The Al and CNTs/Al composites have a disk shape with a diameter of 13 mm and a thickness of 1 mm. The density and BET surface area of the sintered Al were measured using the Archimedes method, and the BET N2-adsorption method to investigate the effect of the surface area of Al on the hydrogen generation rate. The hydrogen generation rate was measured in 75 ml of 10 wt. % NaOH solution at room temperature using a mass flow meter (MFM). The microstructure of the CNTs/Al composite was analyzed by scanning electron microscopy (SEM) after etching in 10 wt. % NaOH solution. The composition of the byproducts after the hydrolysis reaction was characterized by X-ray diffraction (XRD). The composition of the hydrogen gas generated from the hydrolysis of CNTs/Al composites was measured by gas chromatography (GC, Agilent 6890N). The feasibility of using the hydrogen gas generated from the hydrolysis of CNTs/Al composite potential in a PEMFC was investigated via a single PEMFC test. A single PEMFC was assembled with a commercial membrane electrode assembly (MEA, GORE™), gas diffusion layer (GDL), graphite bipolar plates, and aluminum end plates. The active area of the MEA was 5 × 5 cm²; Pt loading in the catalyst layer was 0.4 mg cm⁻². The MEA of the single cell was activated at 0.4 V for 24 h in a hydrogen and air atmosphere (1:2) with 100% relative humidity. After the activation, the hydrogen generation reactor was directly connected to the anode inlet of the single cell. To characterize the electrochemical performance of the single cell, current – voltage (I–V) measurement was performed.

Results and discussion

Effect of CNT content on hydrogen generation rate

Fig. 1 shows a sample of the 5 vol. % CNTs/Al composite fabricated by SPS at 50 MPa of uniaxial stress; the composites SEM morphology is also shown. Evidently, the CNT clusters were randomly dispersed in the Al matrix. Fig. 2 shows the effects of CNT content on the surface morphology of the CNTs/Al after chemical etching in a 10 wt. % NaOH solution. Evidently, the CNTs/Al composite became more porous with increase of the CNT content; hence, the 5 vol.% CNTs/Al composite has the most porous structure among the prepared sample. Fig. 3 shows the effects of hydrolysis time on the accumulated hydrogen volume per unit weight for 0–5 vol. % CNTs/Al composites. The hydrogen generation rate of the CNTs/Al composite increased with increases in the CNT content in the Al matrix as shown in Table 1. The hydrogen generation rate of the 5 vol. % CNTs/Al composite was 40 ml/min g which is 2 times higher than that of the SPSed Al without CNTs. Furthermore, due to its porous structure and large reaction area the SPSed Al has a hydrogen generation rate that is higher than that of the casted Al. Fig. 4 provides the SEM images showing the change in surface morphology of the 5 vol. % CNTs/Al composite according to the hydrogen generation rate of the hydrolysis reaction in 10 wt. % NaOH solutions. Pores and pits rapidly formed in the 30 s – hydrolysis process. As can be seen in Fig. 4b), pores with diameters of about 3–5 μm, emerged at after the 3 min hydrolysis process. The pores grew in diameter and depth during the hydrolysis of the CNTs/Al composite due to severe dissolution of the Al matrix. Fig. 4c) shows that after 10 min of hydrolysis, the pores grew to have diameters in the range of 50–100 μm Fig. 4d) shows that after 20 min, almost all of the Al matrix had corroded away after the hydrolysis; however, CNT clusters remained in the composite because they were stable in the
alkaline solution. Each CNT acts as a localized cathode in the Al matrix during hydrolysis, and hence causes rapid hydrogen generation due to the galvanic corrosion effect between the CNTs and the Al matrix. The hydrolysis of the CNTs/Al composite may produce undesirable carbon based compound such as carbon monoxide (CO) via the reaction of C in CNT and water. Fig. 5 provides XRD patterns for the byproducts after hydrolysis of the 5 vol. % CNTs/Al composite. It is evident that no carbon compounds were formed in the hydrolysis process. By adsorbing on the surface of Pt catalyst CO in hydrogen has a poisoning effect on PEMFC performance[20–22]. For this reason, the purity and composition of hydrogen gas generated from the hydrolysis of CNTs/Al composite was confirmed by GC before the single cell test. Table 2 clearly shows that the hydrogen produced from the hydrolysis of CNTs/Al composite is very pure without any CO gas.

Effect of specific surface area on hydrogen generation rate

Pure Al samples were fabricated by SPS at different levels of uniaxial stress (20, 30, 50 MPa) to investigate the effects of specific surface area on the hydrogen generation rate. Table 3 shows the measured relative density, BET specific surface area, and shrinkage for Al samples processed at different levels of applied stress during SPS. The shrinkage is measured by the decrement in thickness of the samples between the initial powder mixture and the final sintered Al. The relative density was derived by assuming 2.7 g/cm³ as the theoretical density of Al. The shrinkage and the relative density increased with increasing applied stress whereas the BET specific surface area of the SPS processed Al increased with decreasing applied stress. The BET specific surface area of the SPS processed Al at 20 MPa is 1.0663 m²/g. This value is five times
larger than that of the SPS processed Al at 50 MPa (0.2176 m²/g). A porous Al structure with high specific surface area can be achievable by applying a low stress during SPS process. As can be seen in Fig. 6, the hydrogen generation rate of Al decreased with increasing stress applied in the SPS process. Porous Al with higher specific surface area produced fast hydrogen generation from the hydrolysis of Al in alkaline solution. The initial stage hydrogen generation rate of the Al reached the maximum value earlier when the applied stress in the SPS process was 20 MPa due probably to the loosened structure with higher BET area and low density. Fig. 7 shows the influences of the applied stress on the surface morphology of the 5 vol. % CNTs/Al composite formed using the SPS process and then exposed to 10 min - hydrolysis in 10 wt. % NaOH solution. Both of the CNTs/Al composites show a porous morphology due to the dissolution of the Al matrix during hydrolysis. However the CNTs/Al composite formed with 20 MPa applied stress (Fig. 7(b)) was more severely corroded than that formed with 50 MPa applied stress; hence, most of the Al matrix was dissolved. Due to its large specific surface area, the 5 vol. % CNTs/Al composite formed at lower stress (20 MPa) had a corrosion rate that is much higher than that of the composite formed at 50 Mpa. The 5 vol. % CNTs/Al composite formed with 20 MPa exhibited hydrogen generation rate of 120 ml/min g, which is 3 times higher than that of the 5 vol. % CNTs/Al composite formed at 50 MPa, as can be seen in Fig. 8(a). The hydrogen generation of CNTs/Al is lower than that of Al powders (216 ml/min g); however, this is much higher than that of the Al bulk state (maximum 26 ml/min g) [7]. Fig. 8(b) shows the hydrogen generation rate of the 5 vol. % CNTs/Al composite for different levels of applied stress. The hydrogen generation rate was derived from the differential of

![Graph showing hydrogen generation rates of different Al composites](image)

**Fig. 3 –** The effects of porosity and CNTs on the accumulated hydrogen volumes per unit weight at initial stage of CNTs/Al composites.

| Table 1 – Hydrogen generation rates of 0–5 vol. % CNTs/Al composite from the hydrolysis in 10 wt. % NaOH solution at room temperature. |
|-----------------|-----------------|-----------------|
|                 | Al              | 2 vol.% CNTs/Al | 5 vol.% CNTs/Al |
| H₂ generation   | 20              | 30              | 40              |
| rate (ml/min g) |                 |                 |                 |

![SEM images](image)

**Fig. 4 –** SEM images of 5 vol. % CNTs/Al after hydrolysis for (a) 0 s, (b) 30 s, (c) 10 min, (d) 20 min in a 10 wt. % NaOH solution at room temperature.
the accumulated hydrogen volume per unit weight. The hydrogen generation rate of the 5 vol. % CNTs/Al composite at 50 MPa was 40 ml/min g, and lasted for 50 min with 0.3 g. In contrast, the hydrogen generation rate of the 5 vol. % CNTs/Al composite formed at 20 MPa is 120 ml/min g; the produced hydrogen consumed in 20 min due to the faster hydrogen generation rate. A stable hydrogen generation rate above 120 ml/min g was maintained after 2 min of hydrolysis. Table 4 summarizes the hydrogen generation rate of the SPS processed Al and CNTs/Al composite. It is evident from the data shown in Tables 3 and 4 that the hydrogen generation rate of the CNTs/Al composite increases with the increase the composites’s BET specific surface area. The hydrogen generation rate was doubled as a result of galvanic corrosion after CNT additions, and increased 3 times due to the porous Al matrix, which had a large reaction area. In other words, increments of the hydrogen generation rate are caused by the effects of the 60% of larger reaction area, and the 40% higher level of galvanic corrosion. Finally, to achieve rapid hydrogen generation, the 5 vol. % CNTs/Al composite with 20 MPa applied stress was found to be the optimum CNTs/Al composite.

### PEMFC operation

Fig. 9(a) shows the current–voltage (I–V) curves of a PEMFC single cell that was operated by supplying two kinds of hydrogen. The blue curve is the I–V curve of commercial high purity hydrogen; the black curve is the I–V curve of hydrogen generated from the hydrolysis of the 5 vol. % CNTs/Al composite in a 10 wt. % NaOH solution. The cell voltage was 0.72 V at 10 A when hydrogen from the hydrolysis of the 5 vol. % CNTs/Al composite was supplied to the anode of the PEMFC. In the case of supplying commercial hydrogen, the cell voltage was 0.74 V for identical current, confirming the good application of the 5 vol. % CNTs/Al composite as a hydrogen source.

### Table 2 – GC analysis results of the gas generated from the hydrolysis of the 5 vol. % CNTs/Al composite in 10 wt. % NaOH solution. Component mole fractions in the gas were measured by GC.

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>CO₂</th>
<th>CO</th>
<th>CH₄</th>
<th>N₂</th>
<th>O₂</th>
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<tr>
<td>1</td>
<td>98.54</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>98.36</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>3</td>
<td>99.70</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>4</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Aver.</td>
<td>99.55</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

### Table 3 – BET specific surface area, relative density, and shrinkage during the SPS process of the SPSed Al at different levels of applied stress.

<table>
<thead>
<tr>
<th>SPsed aluminum</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied pressure (MPa)</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Shrinkage (mm)</td>
<td>1.37</td>
<td>1.51</td>
<td>1.71</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>89</td>
<td>92</td>
<td>95</td>
</tr>
<tr>
<td>BET specific surface area (m²/g)</td>
<td>1.0663</td>
<td>0.5985</td>
<td>0.2176</td>
</tr>
</tbody>
</table>

Fig. 5 – XRD patterns of the byproducts after the hydrolysis of the 5 vol. % CNTs/Al composite.
for PEMFC. These results demonstrate that the hydrogen generated from the hydrolysis of the 5 vol. % CNTs/Al composite is as pure as commercial hydrogen. Fig. 9 (b) shows the cell voltage curves at constant loads of 10 A, and 20 A when hydrogen from the hydrolysis of the 5 vol. % CNTs/Al composite was supplied to the anode of PEMFC. At a constant load of 10 A, the cell needs hydrogen to be supplied to the anode at a rate of 96 ml/min; air must be supplied at a rate of 299 ml/min. The cell voltage exhibited a stable value of approximately 0.73 V at 10 A for 13 min. However, the cell voltage decreased to 0.4 V after 12 min and then dropped to 0 V. This drop can be attributed to the fact that hydrogen generation rate dropped to below 96 ml/min after 13 min. The hydrogen generated from the hydrolysis of the 3.5 g CNTs/Al composite produced a current of 10 A, for 12 min. Previous PEMFC operation tests using the Al-hydrolysis system were performed only at 10 A, because the hydrogen generation rate is too low to achieve higher current [23,24]. In this work, to take a best advantage of rapid hydrogen generation rate from the hydrolysis of the 5 vol. % CNTs/Al composite, a single cell test was conducted at the high current of 20 A. The cell needs a hydrogen supply rate of 198 ml/min to the anode; a further supply of air at a rate of 611 ml/min to the cathode is necessary to operate at 20 A of current. The cell voltage was maintained at 0.65 V for 6 min at 20 A. After that, the cell voltage decreased to 0.4 V for 45 s and then dropped to 0 V. This may be because the hydrogen generation rate decreased to below 611 ml/min. Therefore, on-board hydrogen production using the hydrolysis of the CNTs/Al designed in this study could be used as a fast hydrogen generation source for PEMFC operation.

Fig. 7 – SEM images of the 5 vol. % CNTs/Al composites at different levels of the applied stress during the SPS process (a) 50 MPa, (b) 20 MPa, after 10 min hydrolysis in 10 wt. % NaOH solution at room temperature.

Fig. 8 – (a) Accumulated hydrogen volume per unit weight, (b) hydrogen generation rates of the 5 vol. % CNTs/Al composite at different levels of the applied stress during the SPS process, in 10 wt. % NaOH solution at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs contents (vol.%)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Applied pressure (MPa)</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>H2 generation rate (ml/min g)</td>
<td>63</td>
<td>51</td>
<td>20</td>
<td>122</td>
<td>40</td>
</tr>
</tbody>
</table>
Conclusions

CNTs/Al composite was fabricated using the SPS method to achieve a rapid hydrogen generation rate in an alkaline solution. A maximum hydrogen generation rate of 120 ml/min g was obtained for 5 vol. % CNT addition and applied stress of 20 MPa. This is 6 times faster than the rate of SPS processed Al without CNT. The fast hydrogen generation rate can be attributed to the large specific surface area of the porous Al matrix, and galvanic corrosion between the CNTs and the Al matrix. The hydrogen generated from the hydrolysis of the CNTs/Al composite has high purity without any production of undesirable CO. A PEMFC operated using the hydrogen gas generated from the hydrolysis of the 3.5 g – CNTs/Al composite produced electricity at 10 A at 0.73 V for 13 min, which is equivalent to 1.6 Wh. Hence, the CNTs/Al composite can be effectively used as a promising hydrogen source for PEMFCs.

References


