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Applications of Recycled Materials to Fuel Cell and Related Technologies

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Here reported are technical applications of two post-consumer materials to developing portable fuel cells. The first is a separator fabrication using woodceramics produced from plant wastes. We succeed to fabricate separators with optimizing manufacturing conditions estimating electrical resistance, density and process fitness. The other is hydrogen generation by means of mechanochemical reactions of Al particles with water. Wasted Al curls are crushed in pure water to make fine particles smaller than 50 μ m. After a suitable activation treatment, Al particles become intensely reactive with H_2O to generate hydrogen.

Key words: fuel cell, separator, woodceramics, hydrogen generation, aluminum particles

1. INTRODUCTION

New types of woodceramics made of used paper, building's salvage, and plant wastes have been developed[1,2] as an industrial material. It has been understood that whole features of woodceramics are hardly substituted, such as lightness, hardness, low cost, excellence for heat and corrosive resistances, electrical conductance and a great flexural strength. We have been studying applicability of woodceramics to separators for PEFC (polymer electrolyte fuel cell), and accomplished to obtain a suitable performance of them.

On the other hand, aluminum alloys are widely used in industry, where a large mass of cut and shaved Al wastes is produced, which has to be well managed. We have attempted to process wastes of shaved Al curls from automobile industry making fine powder which enables to react with water molecules to generate H_2 gas at 10 – 80℃. This hydrogen source is applicable to PEFC for charging mobile type electronic devices of low power.

2. FABRACATION OF SEPARATORS

Separators for PEFC of 200W are attempted to fabricate with using woodceramics powder mixed with grained phenol and graphite, of which chemical components are given in Table I . It is note that a half of the components is cryptomeria particles and bamboo fiber, and the bamboo is especially effective for enhancing mechanical strength.

Table I Ingredients(%) of woodceramics, phenol and graphite

woodceramics		Graphite	Grained phenol
Cryptomeria particle	Bamboo fiber		
40	10	30	20

The manufacturing process of separators is shown in the following flow chart (Fig.1). We mix the woodceramics with graphite and resin for the fabrication choosing six different manufacture conditions such as component ratio, fill weight and molded pressures.

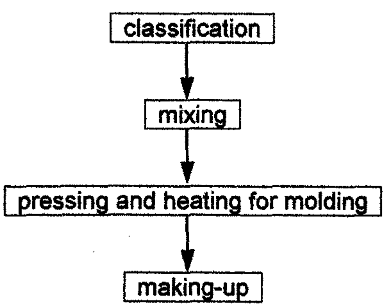

Fig.1 manufacturing process for separators

We can thus control the density of samples in various ways. These conditions denoted by I-VI are given in Table II. The fill weight signifies the amount of a used mixture, when it is compressed.

Table II fabrication conditions of separators (A: woodceramics; B: graphite; C: resin)

No.	Components A : B : C	Fill weight g	Molded pressure kg/cm^2
I	80:0:20	3	240
II	40:40:20	3.6	240
III	40:40:20	3.9	480
IV	40:40:20	4.2	1080
V	20:60:20	4.2	240
VI	40:40:20	4	240

Table III Density, electrical resistance and appearance of separators after molding

No.	Appearance	electrical resistance mΩ	density kg/cm^2
I	good	33.04	1.14
II	good	26.87	1.37
III	NG	—	—
IV	NG	—	—
V	NG	—	—
VI	good	28.20	1.57

After making $\phi 30 \times 2$ samples with different components of I ~VI, their apparent shapes are first checked and electrical resistance and densities are measured as given in Table III. It is found that the compactibility of separators for shaping depends strongly on ratios of the three components. In samples III, IV, V, convex deformations are observed, and in I, II, VI, straight and smooth surface structures are confirmed, and further, lower electric resistances are measured as well. The electrical resistance normalized by that of a graphite separator is shown in Fig.2 for samples I, II and VI. The relative resistance becomes higher than that of a conventional separator consisting of graphite (80%) and resin (20%). It is emphasized that increasing the concentration of woodceramics, higher is the resistance, and in the case of an equal concentration of woodceramics, the resistance decreases with increasing graphite.

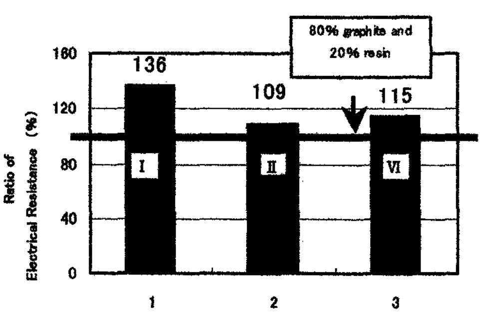

Fig.2 Resistance variation of woodceramics depending upon components

We then fabricate separators under conditions of II. Pictures of a separator with size of 100×100×9 are shown in fig. 3. A groove structure is manufactured with the pitch of 2mm.

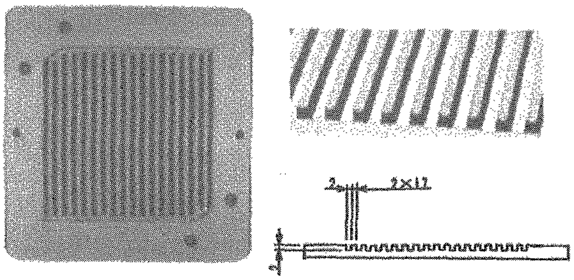

Fig. 3 Pictures of a separator with condition II

3. H_2 PRODUCTION FROM AL WASTES

Metallic aluminum is by nature reactive with water molecules producing H_2, $Al(OH)_3$ and AlH_3. We have devised a method to make reactive Al particles from an Al waste preventing the surface from oxidation. Shaved Al curls from industry are treated according to the following diagram.

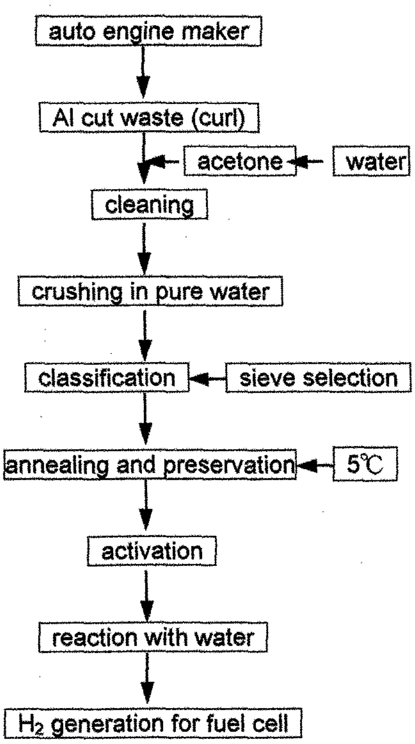

Fig. 4 block diagram for treatments of Al curls

Al curls are crushed in water to make fine powder of 5 to 50 μm. This mechanical process creates microcracks in Al particles, where H_2O molecules can penetrate into and are decomposed to produce AlH3 and AlO in such ways[3, 4],

$$3Al + 3H_2O \rightarrow Al_2O_3 + AlH_3 + (3/2)H_2 \quad (1)$$

or

$$3Al + 2H_2O \rightarrow 2AlO + AlH_3 + (1/2)H_2 \quad (2)$$

The above reactions can be characterized by mechanochemical reactions taking place in cracks, where the mechanical energy inflicted is stored in the Al crystal around cracks. SEM observation reveals particles being irregularly shaped, and larger particles looking like aggregates of small particles of about 5 μm as shown in Fig. 5.

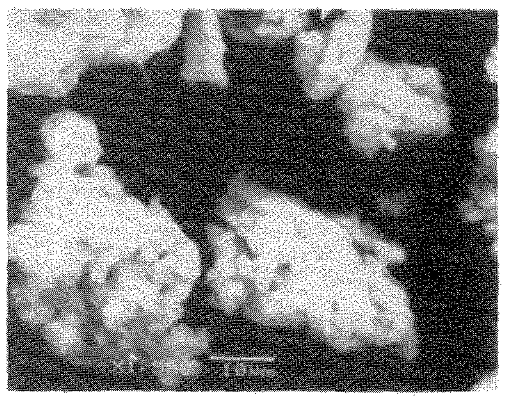

Fig. 5 SEM picture of Al particles

It is required to control starting the reaction and the rate of H_2 production. We have developed a method of giving thermal and supersonic shocks to activate the Al particles to begin a rapid H_2 generation. After the activation the particles had better be kept in water at 20℃ for 1 to 2 days. This annealing process creates and extends possibly nanocracks all over the particles, which enable them to generate intensively hydrogen gas.

Fig. 6 depicts rates of H_2 production of Al particles of 10g as a function of reaction time. It is noted that the reaction rate depends strongly on temperature, and production rates are 0.12 and 6.0 ml/min·g at 20 and 60 ℃, respectively.

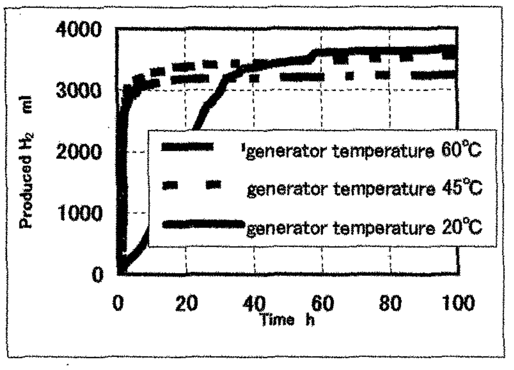

Fig.6 Production rates of hydrogen gas

4. DISCUSSION

4-1. Separators made of woodceramics

Although we observed some increases in electrical resistance of our separators with increasing the amount of woodceramics, we may still remain unknown ways to optimize the resistance and better qualities with suitable distributions of the three components. Especially, a good amount of graphite becomes important when woodceramics is mixed. For samples Ⅲ, Ⅳ and Ⅴ in Table Ⅱ, we assign NGs due to crack formations in separators. For a further improvement, we consider to utilize finer particles of woodceramics and to give thorough mixing among woodceramics, graphite and resin. An over usage of graphite finds to decrease in the electrical resistance similar to conventional carbon separators in compensation for other important properties. We have made durability tests for our separators and are convinced that they can keep suitable resistances against heating to 130℃ for 500hr, and against the full humidity at 60℃ for 500 hr.

4-2. Al wastes for H_2 production

The overall reaction of Al with H_2O is given by

$$3H_2O + 2Al \xrightarrow{\text{mechanochemical}} 3H_2 + Al_2O_3 \qquad (3)$$

while production of hydrogen from methanol for mobile FC's (DMFC) is given by

$$H_2O + CH_3OH \xrightarrow{\text{catalytic}} 3H_2 + CO_2 \qquad (4)$$

The both reactions are apparently similar, though the reaction mechanisms differ totally, and reaction temperatures differ from each other at 20℃ and 200℃, respectively. The amount of H_2 production is about 350ml/g obtained in Fig. 6, which is smaller than that predicted in eq. (3). This can be understood by facts that the produced hydrogen contains oxygen molecules by a few percent according to mass spectroscopic analysis, and larger is the oxygen concentration, smaller is the particle size. These facts may imply that the particle surface is partially oxidized during the powder formation in water, and the surface oxygen may reacts with produced hydrogen resulting in decreasing H_2 production. It should be emphasized that surface contaminations by metallic ions such as Fe and Cu, and by organic molecules reduce drastically the rate of H_2 generation.

5. CONCLUSION

(1) Using woodceramics we succeed to fabricate separators with fine grooves. This might be the first report in fuel cell science.

(2) The present separator can be characterized in terms of high hardness/density, high flexural strength, long stability/durability, low electrical resistance and low cost.

(3) Al curls of an industrial waste can be converted to hydrogen energy by the present method, which emits no CO_2 gas at all.

(4) A new technology of hydrogen generation is established by means of decomposing water molecules at room temperature.

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