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Opinion

Material Aspects Pertaining to Hydrogen Production from Aluminum: Opinion

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Opinion

Background

The use of lightweight metals as hydrolyzing materials for hydrogen (H_2) generation has attracted much attention in recent years. This is clearly evident when one considers the continuous stream of publications being made available in the public peer-reviewed domain on the subject. Metal-based hydrolyzing materials are combined with water, under certain conditions, to allow the hydrolysis reaction, yielding high-purity H_2 on demand. Of the lightweight metals investigated, aluminum (Al) has shown significant potential as it is lightweight, relatively inexpensive, and abundant.

Reaction mechanisms

The complete hydrolysis of Al yields 1.36 L H_2 per g Al under standard atmospheric conditions, according to the following reactions:

$$2Al+4H_2O=2AlO\,(OH)+3H_2$$

$$2Al+6H_2O=2Al\,(OH)_3+3H_2$$

However, the hydrolysis of Al is prevented by a thin, coherent oxide layer on the surface of Al, which prevents contact between the underlying metallic Al and water. This oxide layer is generally removed via the following routes: (i) exposure to solution of extreme pH, ii) amalgamation with mercury/gallium, iii) thermal homogenization with certain metals (typically with metals with melting points below that of Al), and iv) mechanochemical processing with water soluble salts, metal oxides and/or certain metals (e.g., gallium, zinc, tin, indium, and/or bismuth). Of these methods, it is the mechanochemical processing of Al, which does not require the use of corrosive liquids and expensive/toxic elements, that appears most favorable. Advantages of its application include user/environmental friendliness and relatively low fabrication costs.

Mechanochemically processed Al

HySA Infrastructure (South Africa) has undertaken the fabrication of mechano-chemically processed Al composites using various activation compounds: bismuth, tin, and/or indium. These composites are highly reactive towards neutral pH water of various qualities (e.g., tap, filtered, deionized) [1-5]. Mechanochemical processing facilitates particle size reduction of the composite particles and the distribution of activation compounds throughout Al particles. When exposed to water, a large surface area and numerous microgalvanic cells between anodic Al and cathodic activation compounds affords these composites with high hydrolysis activity-yields of >99% H_2 are achieved. Figure 1 illustrates the change in morphology of Al before and after processing.

The H_2 generated from the hydrolysis of mechanochemically processed Al may be combined with proton exchange membrane fuel cells (PEMFCs) to convert the chemical energy of H_2 into an electrical current. Because of the high purity of the generated hydrogen (more specifically, the absence of platinum-catalyst-poisoning carbon monoxide), its direct application in PEMFCs is acceptable without concern for catalyst degradation. The complete hydrolysis of 1kg of Al may generate the energy equivalent of approximately 4.4kWh worth of H_2-approximately 50-60% of which may be converted to electrical energy (depending on the efficiency of the relevant PEMFC) [6,7]. A possible real-world application includes refueling of PEMFC-powered unmanned aerial vehicles (UAVs) in the field. A 16kg battery-powered UAV has an operational capacity of 5h, whereas a similar PEMFC powered system consuming gaseous or liquid H_2 can operate for 24 to 48h [8]. A recent report by the US Army states the following: "The U.S. Army Research Laboratory plans to license its discovery of a nano-galvanic aluminum powder for H_2 generation" [7]. The reasoning behind this is likely due to the low noise emissions of fuel cells, allowing stealthier operations. In addition to this, the relatively easy heat management of such a system can afford vehicles with low infrared signatures, when compared to traditional internal combustion engines used in military vehicles.

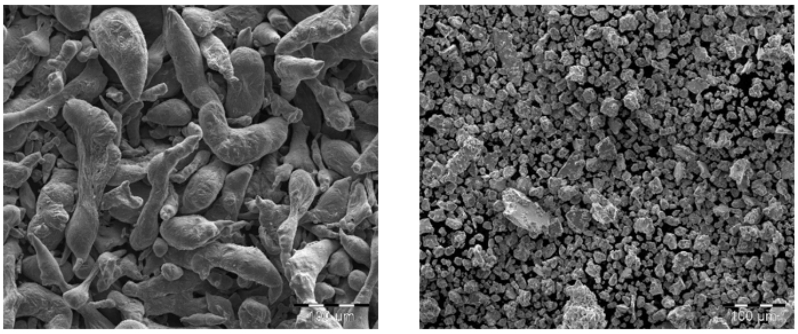

Figure 1: Field emission scanning electron microscopy images of Al particles: (a) before and (b) after mechanochemical processing using bismuth, tin, and/or indium as activation compounds.

Challenges

However, it is likely that suitable high-capacity reactor designs have yet to be realized as the hydrolysis of Al releases an appreciable amount of heat, which has a significant effect on the hydrolysis reaction kinetics. Al's hydrolysis is significantly accelerated by *in-situ* generated reaction heat and it may cause operational complications. In addition to this, hydrolysis products (AlO(OH) and/or $Al(OH)_3$) precipitate as a gel-like substances that may result is reactor complications, such as blockages.

Considering the energy required to convert Al hydroxides to alumina, and alumina to Al metal via the Hall-Heroult process, H_2 generation from the hydrolysis of Al is a niche application. Nevertheless, this H_2 generation route has significant potential for on-site and on-demand energy vector generation. It is recommended that further research into developing up-scaled processes for Al composite fabrication, fit-for-purpose reactors, and real-world applications should be carried out in the future.

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