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Polymer electrolyte membrane fuel cell using hydrogen produced by waste aluminum hydration reaction

조선대학교 대학원

첨단에너지자원공학과

장 희 원

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폐알루미늄 수화반응으로부터 생성된 수소를 이용한 고분자전해질 연료전지

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As global warming becomes more and more severe and abnormal climate events occur frequently, efforts to lower the global average temperature rise are taking place worldwide. As a result, hydrogen is receiving much attention in various fields as a new potential candidate to replace fossil fuels as a future next-generation energy source. It is emerging as the core of carbon-neutral policy. However, about 75% of the world's hydrogen comes from natural gas reforming, generating carbon dioxide, and is a problem. In addition, high production, storage, and transportation costs are also a problem in the existing hydrogen industry.

In this study, hydrogen was produced through a waste aluminum hydration reaction and directly supplied to a polymer electrolyte membrane fuel cell (PEMFC) to determine whether it was suitable as a fuel and to confirm the possibility of hydrogen production. The aluminum used in this study is UBCs (used beverage cans, A3104), de-coated aluminum can granules (A3104, A5182), construction aluminum materials (A6063), yogurt lids (A8011), and high-purity aluminum with a purity of 99.99%. To analyze the characteristics of the membrane electrode assembly (MEA) after operating the fuel cell using aluminum hydration reaction-based hydrogen, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed.

The waste aluminum hydration reaction was performed with 5 g of waste aluminum and 200 ml of 1, 3, and 5 M NaOH aqueous solution. The hydrogen production was 6435, 6630, 6540, 5124, and 6855 mL. The temperature rose to 43, 79, 40, 63, and 63 ℃ respectively, when 5 g of UBCs, de-coated Al can granules,

construction aluminum materials, yogurt lids, and high-purity aluminum were added to 5 M NaOH solution. In the 3 M NaOH solution, hydrogen was produced in 6270, 6480, 6540, 4950, and 6710 mL, respectively, and the temperature rose to 38, 76, 37, 55, and 32 ℃.

In the application of PEMFC, using conventional high-purity hydrogen (99.999%), the current density at 0.6V was reduced from 1.25 A/cm^2 to 1.20 A/cm^2 after 200 cycles, UBCs was reduced from 1.21 A/cm^2 to 0.33 A/cm^2, de-coated Al can granules were reduced from 1.09 A/cm^2 to 0.54 A/cm^2, construction aluminum materials were reduced from 1.20 A/cm^2 to 1.01 A/cm^2, yogurt lids were reduced from 1.20 A/cm^2 to 0.25 A/cm^2, and high-purity aluminum was reduced from 1.27 A/cm^2 to 1.23 A/cm^2. Compared to high-purity hydrogen (99.999%) and other waste aluminum hydration reaction-based hydrogen, significant performance degradation did not occur in cyclic voltammetry (CV) except UBCs and yogurt lids. Unlike other waste aluminum in this experiment, it is considered that the polymer coating on UBCs and yogurt lids directly damage the fuel cell's membrane electrode assembly (MEA), affecting durability. Also, in electrochemical impedance spectroscopy (EIS), the hydrogen-based on UBCs and de-coated Al can granules have high impedance and are greatly affected by charge transfer.

Hydrogen generated from construction aluminum materials had a high concentration of more than 99%, so its initial operating performance was similar to that of a high concentration. However, most waste aluminum hydration reaction-based hydrogen showed more degradation than conventional high-concentration hydrogen when applied to PEMFC operation. Especially, waste aluminum with polymer coating is more degraded, so it is essential to install additional devices to increase the concentration of waste aluminum-based hydrogen gas before supplying it to PEMFC. As a result, if hydrogen production through pretreatments of waste aluminum or a process of removing impurities after hydrogen production is performed, it can be an economical and effective alternative to fuel supply for fuel cells.

Abstract

Polymer electrolyte membrane fuel cell using hydrogen produced by waste aluminum hydration reaction

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지구 온난화가 심화되면서 이상기후 현상이 빈번하게 발생하고 있으며, 이에 따라 지구 평균기온 상승을 낮추기 위한 노력이 전 세계적으로 진행되고 있다. 수소는 미래 차세대 에너지원으로 화석연료를 대체할 새로운 잠재적 후보로 다양한 분야에서 많은 주목을 받고 있으며, 탄소중립 정책의 핵심으로 떠오르고 있다. 현재 전 세계 수소의 약 75%가 천연가스 개질을 통해 생산되며, 생산 시 발생하는 이산화탄소를 비롯한 생산, 저장 및 운송 비용이 문제가 되고 있다.

본 연구에서는 폐알루미늄과 물의 수화반응을 통해 생산된 수소를 고분자 전해질막 연료전지(PEMFC)에 직접 연료로 공급하여 폐알루미늄의 수소 생산 가능성과 연료전지에 대한 적합여부를 확인하였으며, 알루미늄은 일상생활에서 쉽게 접할 수 있는 알루미늄 캔 (used beverage cans, UBCs), 탈 코팅된 알루미늄 캔 그래뉼 (de-coated Al can granules), 건설용 알루미늄 (construction aluminum materials), 요구르트 뚜껑 (yogurt lids), 고순도 알루미늄 (high-purity aluminum)를 이용하였다. 또한, 연료전지 구동 후 막전극접합체(MEA)의 특성을 분석하기 위해 순환전압전류법(CV), 전기화학적 임피던스 분광분석법(EIS)을 수행하였다.

폐알루미늄 수화반응은 각 종류의 폐알루미늄 5 g과 1, 3, 5 M NaOH 수용액 200 mL로 수행하였다. UBCs, de-coated Al can granules, construction aluminum materials, yogurt lids 및 high-purity aluminum과 5 M NaOH 수용액과 반응했을 때, 각각 6435, 6630, 6540, 5124, 6855 mL의 수소가 발생했으며, 온도는 43, 79, 40, 63, 63 ℃까지 상승하였다. 3 M NaOH 수용액의 경우 수소가 6270, 6580, 6480, 4950, 6710 mL의 수소가 발생했으며, 온도는 38, 76, 37, 55, 32 ℃까지 상승했다.

수화반응을 통해 발생된 수소를 PEMFC에 적용하여 200 Cycle 전후로 전류밀도를 측정한 결과, high-purity hydrogen (99.999%)를 사용했을 때 0.6V의 전류밀도

가 1.25 A/cm^2에서 1.20 A/cm^2로 감소하였고, UBCs는 1.21 A/cm^2에서 0.33 A/cm^2로 감소하였다. de-coated Al can granules은 1.09 A/cm^2에서 0.54 A/cm^2로, construction aluminum materials은 1.20 A/cm^2에서 1.01 A/cm^2로, yogurt lids은 1.20 A/cm^2에서 0.25 A/cm^2로, high-purity aluminum은 1.27 A/cm^2에서 1.23 A/cm^2로 감소했다. high-purity hydrogen (99.999%) 및 기타 여러 종류의 폐알루미늄 수화반응 기반 수소와 비교하여 순환전압전류법(CV)에서 UBCs 및 yogurt lids을 제외하고는 큰 성능 저하가 발생하지 않았다. 본 실험에서 다른 폐알루미늄과 달리 UBCs와 yogurt lids에 코팅된 폴리머는 연료전지의 막전극접합체(MEA)에 직접적인 손상을 주어 내구성에 영향을 주는 것으로 판단된다. 또한 임피던스 분광분석법 (EIS)에서 UBCs와 de-coated Al can granules 기반의 수소들은 높은 임피던스를 가지며 전하 이동에 크게 영향을 받았다.

Construction aluminum materials에서 생성된 수소는 99% 이상의 고농도를 가지고 있어 초기 운전 성능은 고농도와 크게 다르지 않았으나, 대부분의 폐알루미늄 수화반응 기반 수소는 PEMFC 운전에 적용했을 때 high-purity hydrogen보다 더 많은 열화를 보였다. 특히, 폴리머 코팅된 폐알루미늄은 열화가 심해 PEMFC에 공급하기 전에 수소가스 농도를 높이기 위한 추가 장치 설치가 필수적이고, 폐알루미늄을 전처리하여 수소를 생산하거나 수소 생산 후 불순물 제거 공정을 거치면 경제적이고 효과적인 연료전지 연료 공급 대안이 될 수 있을 것으로 판단된다.

1. Introduction

1.1 Background and objectives

Hydrogen is receiving attention in various fields as a new potential candidate to replace fossil fuels for the next-generation energy source in the future (Balat, 2008; Dincer et al., 2016). The hydrogen is also attracting attention as a means of storing renewable energy and an eco-friendly energy source that can be used in various fields, such as fuel for fuel cell electric vehicle (FCEV) and power plant. In order to achieve the hydrogen economy, which is in the initial stage, the world is entering into a competition to create an ecosystem such as hydrogen production, supply, storage, and utilization.

The Korean government presented a long-term goal of expanding renewable energy in January 2019 and presented its goal of becoming a leading hydrogen economy country by 2040. It includes supplying 6.2 million FCEVs, supplying 17.1 GW of fuel cells, producing more than 5.26 million tons per year, and reducing hydrogen charge price to 3,000 won/kg. And then, they announced the 2050 carbon-neutral promotion strategy and the 5th basic plan for new and renewable energy in December 2020. Therefore, the importance of the relevant fields is becoming more prominent due to these policies.

Hydrogen, which is currently emerging as the core of carbon-neutral policy, is classified into green, blue, and gray hydrogen depending on the production method, and the amount of carbon dioxide generated during the manufacturing process. About 2 million tons of hydrogen are produced annually in Korea, but there is a problem that most of them are byproduct hydrogen and reformed hydrogen that generates carbon dioxide (Kim et al., 2019). Han et al. (2019) analyzed that the amount of CO_2 emitted per hydrogen production of 1 kg by gray hydrogen production technology, which accounts for the majority of domestic hydrogen production, is emitted from 11.39 kg to 15.03 kg (Table 1-1).

Various studies have been conducted to solve this problem, including P2G (Power to Gas) technology. P2G electrolyzes water using renewable energy (wind, solar, etc.) that can not be accommodated in the power system. Moreover, it produces hydrogen or reacts with carbon dioxide to store and use it as a fuel form, such as methane. Also, catalyst manufacturing studies have been conducted to improve the efficiency of the water electrolysis reaction and reduce the price of the catalyst. However, green hydrogen produced by water electrolysis requires a higher energy consumption than input energy, so much research is needed (Park et al., 2020, Chung et al., 2019).

As one of the ways to overcome this problem, hydrogen production through the aluminum hydration reaction can be an alternative to reduce input energy efficiency. When an alkaline solution such as NaOH is added to an aluminum hydration reaction, NaOH does not consume but acts as a catalyst. Also, alkaline water corrodes aluminum and produces hydrogen through a reduction reaction (Hiraki, 2007; Sim et al., 2009). Aluminum is used in various fields in our daily lives due to its lightweight, excellent corrosion resistance, easy casting, and excellent electrical conductivity. Aluminum is used for multiple purposes depending on the alloy composition and various manufacturing methods, so it is often discarded as various types of waste in our daily lives. In the case of scrap-type aluminum with a precise shape, there is no problem with recycling as long as it is collected. However, recycling has many difficulties because various aluminum waste is increasing. Especially the recycling rate of composite aluminum is meager. In some cases, composite aluminum, which is difficult to sort, can be separated into general waste at waste treatment facilities. Recently, most of the composite aluminum, including various food packaging materials in Korea, has been changed to a "hard to recycle" rating, and the recycling standards are becoming stricter. In addition, aluminum consumption is about 1.21 million metric tons as of 2021, showing an average consumption of 1.26 million metric tons from 2011 to 2021. Based on the above, it is expected that a large amount of non-recyclable composite aluminum will generate in the future.

The aluminum hydration reaction has the advantage of reacting sufficiently with waste aluminum and does not require energy for separation because the reaction occurs quickly. The problem of the existing method that requires high energy for hydrogen production can be solved by applying waste aluminum hydration. Therefore, various aluminum wastes were introduced in this study for hydrogen production using a hydration reaction with an alkaline solution. The produced hydrogen was directly supplied into a polymer electrolyte membrane fuel cell to evaluate electrochemical performances.

Table 1-1. CO_2 emissions by gray hydrogen production technology (Han et al., 2019)

Method	Feed Production	H_2 Production Process	Total Amount
NG Reforming	0.02	11.37	11.39
LPG Reforming	unknown	15.03	15.03
Naphtha Reforming	unknown	15.02	15.02

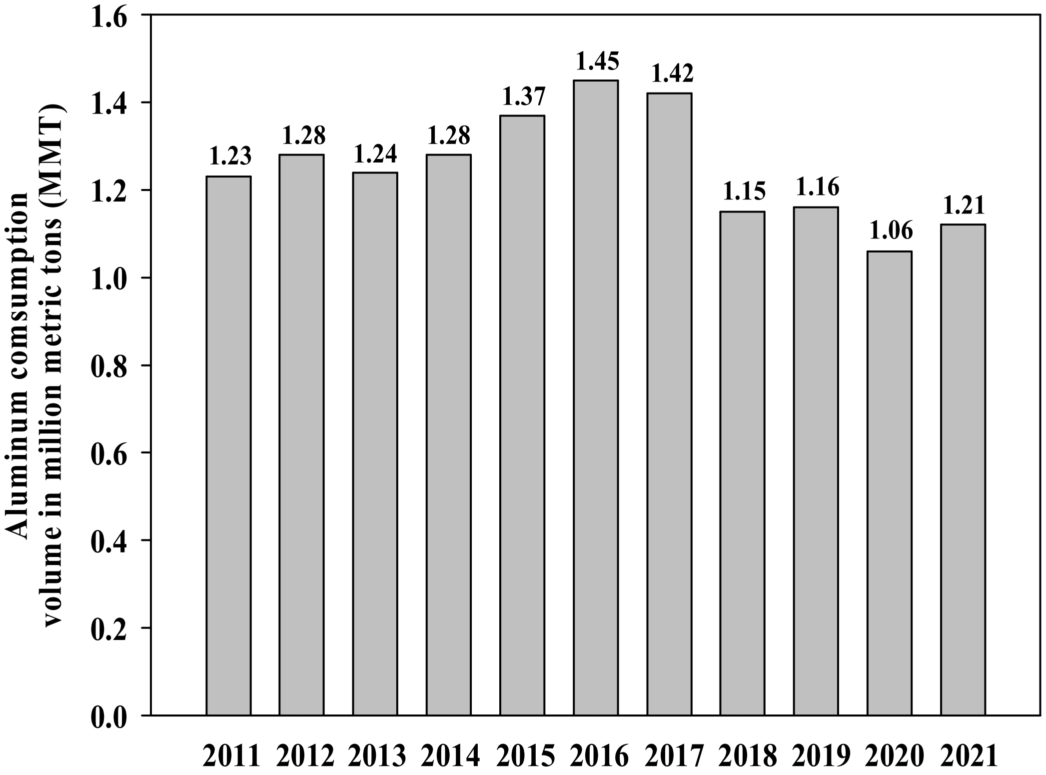


Figure 1-1. Refined aluminum consumption in Korea (2011~2021)

1.2 Research necessity

As global warming becomes more and more serious, abnormal climate events occur frequently, and efforts to lower the global average temperature rise are taking place worldwide. Many countries around the world are working towards the same goal of keeping the average global temperature rise below 2 ℃ and not exceeding 1.5 ℃ (UNFCCC, 2015). Also, they are pursuing a decarbonization strategy that reduces fossil fuel-based energy and uses renewable energy to control global warming. Hydrogen is expected to be the main alternative to the future energy mix.

There is gray hydrogen made by emitting carbon from fossil fuels such as natural gas, blue hydrogen that has collected and removed the emitted carbon, and green hydrogen produced without carbon emissions from renewable energy. The global hydrogen production is about 100 million tons per year and the proportion of hydrogen produced by water electrolysis using renewable energy accounts for about 1%. Production costs are 0.7-2.5 $/kg-H$_2$ for gray hydrogen, 1.2-2.6 $/kg-H$_2$ for blue hydrogen, and 3.2-7.7 $/kg-H$_2$ for green hydrogen (IEA, 2020). Recently, the U.S. Department of Energy (DOE) launched the "Energy Earthshots Initiative." Hydrogen shot, the first of the Energy Earthshots Initiative, aims to reduce the cost of green hydrogen by 80% within one decade to 1 $/kg to revitalize the hydrogen economy (DOE, 2021). Also, International Renewable Energy Agency (IRENA) emphasized that green hydrogen plays a significant role in suppressing the increase in the Earth's average temperature below 1.5 ℃ and derived green hydrogen production costs by region while considering hydrogen demand and land area. In the report, Korea is regarded as a country that is not suitable for green hydrogen production due to mountainous terrain, lack of land, and lack of water. Korea's green hydrogen production price is expected to be 2.9 ~ 4.1 $/kg-H$_2$ in 2050, and China, the most suitable country for green hydrogen production, is expected to be 0.65 ~ 1.1 $/kg-H$_2$ (IRENA, 2022).

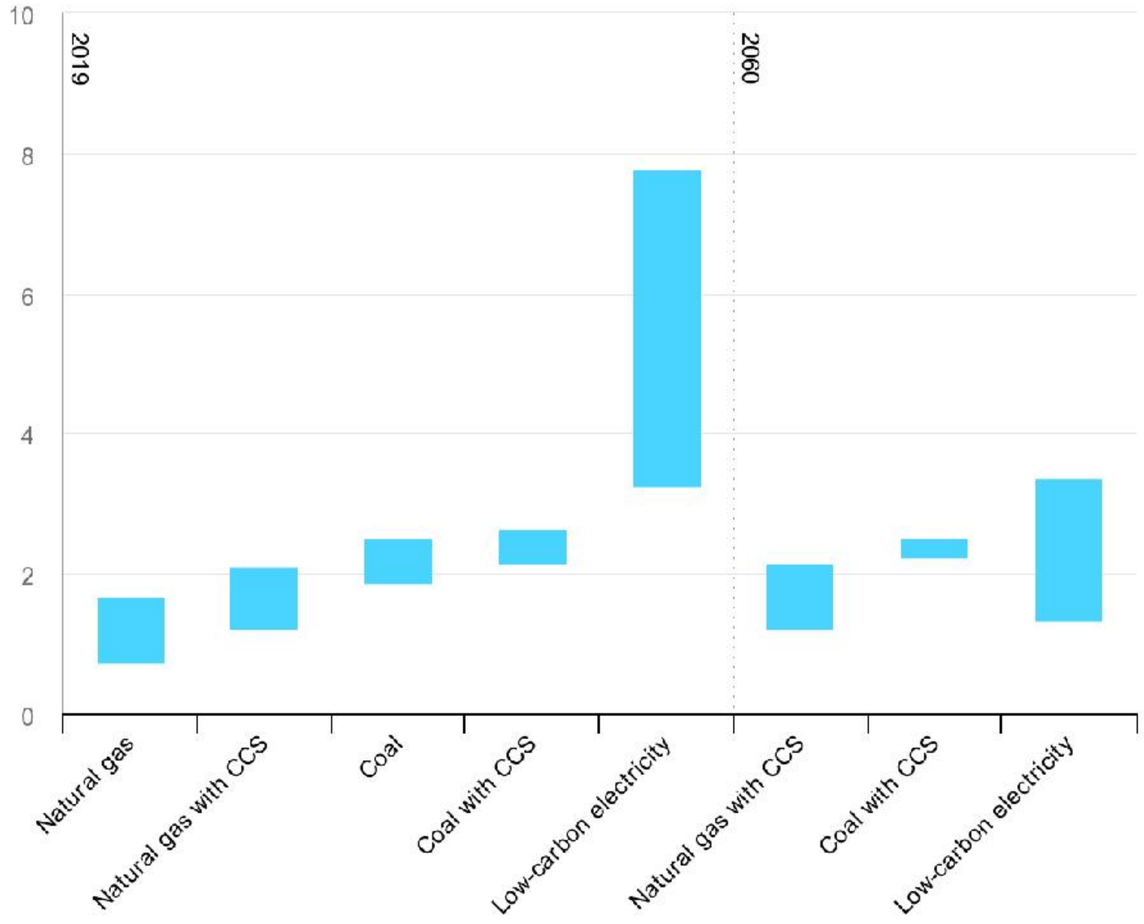


Figure 1-2. Global average levelised cost of hydrogen production by energy source and technology, 2019 and 2050 (IEA, 2020)

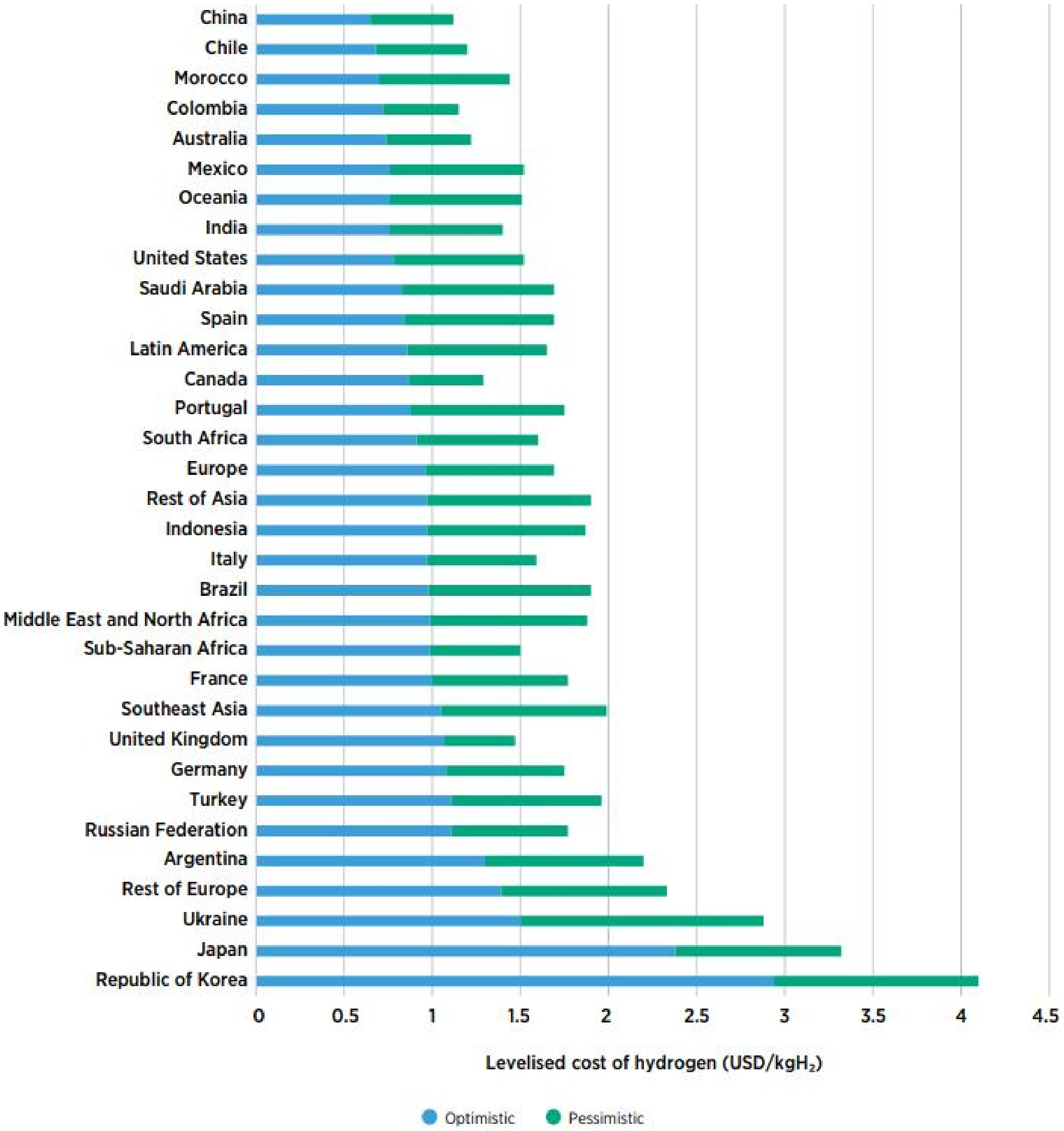


Figure 1-3. Levelised cost of hydrogen range in 2050 derived from supply-demand analysis (IRENA, 2022)

As the IRENA report, green hydrogen production is limited in Korea, so the aluminum hydration reaction can effectively produce an eco-friendly and sustainable hydrogen energy source. Among the earth's crust components, aluminum occupies the most significant proportion, followed by oxygen and silicon. Aluminum around us is closely related to our daily lives and all industrial fields. In addition, aluminum can be easily melted and recycled when it is generated as scrap in a precise shape. However, the recycling rate of composite aluminum is significantly reduced. This composite aluminum is classified as general waste in waste treatment facilities and cannot be recycled.

Recently, the amount of aluminum waste resources (composite packaging materials, films, aluminum cans, solar waste panels, etc.) has increased in Korea. Therefore, there is an increasing need to suggest a way to manage and dispose of aluminum waste. Furthermore, if hydrogen is produced by waste composite aluminum as a raw material, it is possible to reduce the high production cost of green hydrogen. Therefore, it is necessary to establish a hydrogen production system based on an eco-friendly and economical waste aluminum hydration technique.

Hydrogen production is essential for the vitalization of the hydrogen economy, but it is also essential in terms of storage and transportation. The hydrogen economy value chain refers to the cycle from production to storage, transportation, charging, and use of hydrogen. However, green hydrogen production costs are more expensive than other hydrogen production methods, and hydrogen has a low energy density in a gaseous state at room temperature, making it more challenging to store and transport than liquid fuel. Also, about 10-20% of leakage occurs during production, storage, and transportation (Chung, 2019).

Currently, the hydrogen storage and transportation methods used as a commercial class are storage and transportation based on high-pressure gaseous and liquid phases of hydrogen. In Korea, where large-scale hydrogen is not yet prepared, low-pressure pipes are mainly used for short distances, and high-pressure tube trailers are mainly used for medium and long distances. The pipe transportation method is mainly used for a small amount of hydrogen transportation. The cost of pipe construction is cheap compared to others because the consumption site is adjacent to the hydrogen production facility.

Liquefaction, mainly used for liquid hydrogen transport, is a method of cooling hydrogen to -253 ℃ based on atmospheric pressure and transporting it to a tank truck in a liquid state. However, the method of liquefying hydrogen consumes a lot of power and causes greenhouse gas emissions in the liquefaction process. Also, high costs are involved in compression and storage (Choe, 2020). On the other hand, producing hydrogen through the aluminum hydration reaction can easily transport hydrogen as solid-state aluminum and overcome the disadvantages of conventional methods. Besides, it is possible to reduce the amount of greenhouse gas generated in the entire cycle of hydrogen (production – storage – transport-charge-use).

1.3 Research scope

Hydrogen production through the aluminum hydration reaction was studied to get an eco-friendly and sustainable hydrogen energy source. Hydrogen generation amount and rate using waste aluminum and NaOH are measured, and optimal conditions for aluminum hydration reaction are found. In addition, hydrogen gas concentration analysis and direct injection into the polymer electrolyte fuel cell as fuel were attempted to determine whether it is suitable for the polymer electrolyte membrane fuel cell. Finally, the possibility of an aluminum hydration reaction was evaluated to confirm whether it has economic value through the generated by-products.

2. Literature review

2.1 Hydrogen production technologies

Hydrogen can be produced through various processes. For example, there are methods of decomposing natural gas into high-temperature and high-pressure water vapor, separating hydrogen in mixed hydrogen gas from industrial processes, and methods of water electrolysis to produce hydrogen.

2.1.1 Natural gas reforming

About 76% of the world's hydrogen comes from natural gas reforming (IGU, 2020). As a method of producing hydrogen through a steam-methane reforming reaction using high-temperature and high-pressure steam, carbon monoxide is generated in addition to hydrogen during the reaction (2.1). After that, carbon dioxide and additional hydrogen are produced through a water-gas shift reaction (2.2). Hydrogen using natural gas reforming is cheaper than other hydrogen manufacturing methods and is easy to transport because it can utilize an existing gas pipeline.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{2.1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2.2}$$

2.1.2 By-product hydrogen

By-product hydrogen is a method produced by refining the mixed gas containing a lot of hydrogen with pressure-swing adsorption (PSA) to increase the purity of the by-products generated in the process of reforming, decomposing, steelworks, and naphtha. Synthetic gas generated in industrial processes is not converted into high-purity hydrogen and is used to produce other petroleum and petrochemical products when the demand for by-product is insufficient (KEEI, 2021). It is the most common method of producing hydrogen in Korea.

2.1.3 Water electrolysis

Water electrolysis is a method of electrolyzing pure water to produce hydrogen, and representative water electrolysis methods include alkaline water electrolysis (AWE), polymer electrolyte membrane water electrolysis (PEMWE), and solid oxide electrolysis cell (SOEC).

(1) Alkaline water electrolysis (AWE)

Alkaline water electrolysis (AWE) is a technology that electrolyzes water using an alkaline electrolyte. It is currently the most commercialized water electrolysis technology and has an operating condition of 100 ℃ or less. Porous diaphragms and non-precious metal catalysts are used to commercialize them at low cost and with high durability and are driven in an alkaline environment. (Kim et al., 2018). The porous diaphragms use a high-concentration alkali solution as a medium for ion transfer through a porous structure composed of hydrophilic nanoparticles and a polymer binder, not utilizing the ion conductivity of the material itself (Lee, 2022). Generally, a high concentration of 20 to 30 wt% of potassium hydroxide is used as an electrolyte of an alkaline unit cell, and there are a method of configuring the same in series using unipolar electrodes and a method of connecting the cathode electrodes in parallel. Furthermore, effectively preventing the mixing of hydrogen and oxygen gas caused by the porous structure becomes a key in the porous diaphragm for alkaline water electrolysis (Lim, 2021).

(2) Polymer electrolyte membrane water electrolysis (PEMWE)

Polymer electrolyte membrane water electrolysis (PEMWE) uses an ion exchange membrane with no pores and ion conductivity. The unit cell is configured in the form of a membrane electrode assembly. PEMWE is the best compared with other water electrolysis in system miniaturization, maintenance, and repair. However, precious metals (Ti, Pt, Ir, Au) are mainly used in various parts, such as catalysts and porous transport layers in PEMWE. Therefore, it is a main problem to make them commercially viable and competitive in price (Lee, 2022; Lee et al., 2008). Recently, the price and energy efficiency are becoming more similar to AWE, and the PEMWE is expected to be used for renewable energy-based green hydrogen as additional R&D proceeds.

(3) Solid oxide electrolysis cell (SOEC)

Solid oxide water electrolysis cell (SOEC) can be operated under high temperature and high-pressure conditions and have high efficiency. It is a technology that uses a solid oxide electrolyte and electrolyzes steam at a high temperature above 800 ℃ to produce hydrogen. It can produce hydrogen more efficiently while using a relatively small amount of electricity (Lee et al., 2021). SOEC mainly uses a ceramic-based solid oxide electrolyte (Ni-YSZ), so it has excellent corrosion resistance and easy maintenance. However, SOEC needs to be concerned about issues related to lack of stability and degradation before commercialization because it requires an additional heat source to heat water vapor above 800 ℃ and has high-temperature operating conditions (Choi, 2011).

2.1.4 Photocatalysis

A common method of producing hydrogen is separating water molecules into hydrogen and oxygen using electricity, but photo-catalytic water separation is a potentially simpler and more efficient method. Photocatalyst promotes the reduction-oxidation (REDOX) reaction and divides them by using light as an energy source instead of electricity. TiO_2 is mainly used as a representative photocatalyst. When light is irradiated to a TiO_2 single crystal electrode, water is separated into hydrogen and oxygen by photo-oxidation and photo-reduction reactions. The energy required to cause the photoexcitation reaction is about 387.5 nm (3.2 eV) due to excellent physical properties such as sufficient energy from sunlight, chemically stable, excellent photo activity, and harmless to the human body (Guo et al., 2019).

2.1.5 Aluminum hydration

In the aluminum hydration reaction, when an alkaline solution is added, such as NaOH, it is not consumed and acts like a catalyst, while aluminum has a corrosion reaction and water produces hydrogen as a reduction reaction occurs (Hiraki, 2007; Sim et al., 2009). In addition, when aluminum was hydrated in an aqueous NaOH solution, the hydrogen production rate was increased. Moreover, the copper and sulfuric acid mixture significantly increased the hydrogen production rate. When hydrogen was produced by adding aluminum coated in an alkaline KOH aqueous solution and copper powder during a hydration reaction, the effective hydrogen production rate increased by up to 6 times. The effective hydrogen production rate jumped 200 to 250 times when copper was used for compressed aluminum samples (Shmelev et al., 2016). When different metals are in contact with each other in the electrolyte, a potential difference occurs, and a current flows between metals. As a result, highly active aluminum acts as an anode, and other corrosion-resistant metals act as a cathode, resulting in galvanic corrosion in the aluminum hydration reaction (Figure 2-1).

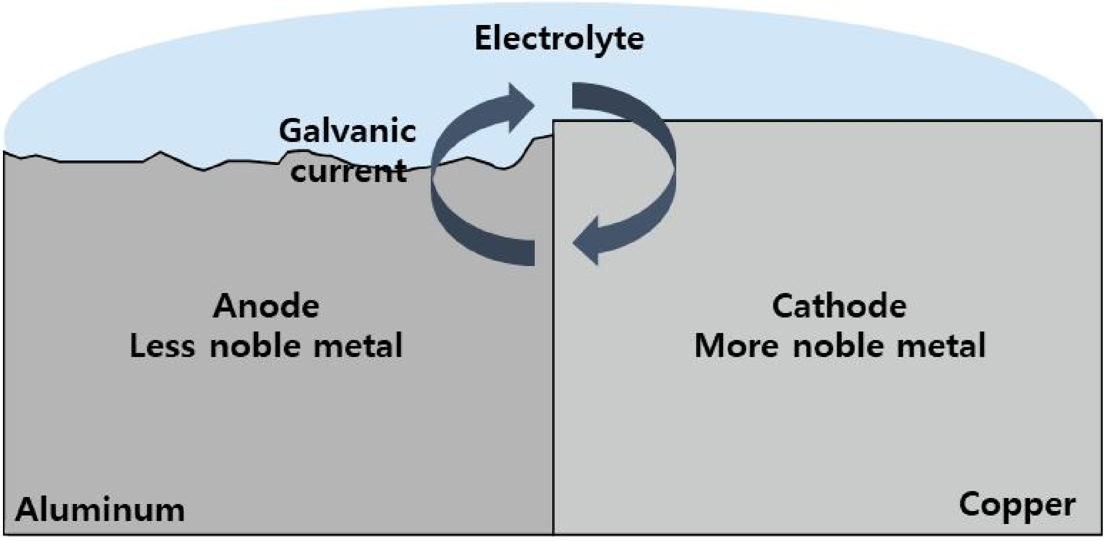


Figure 2-1. The principle of galvanic corrosion

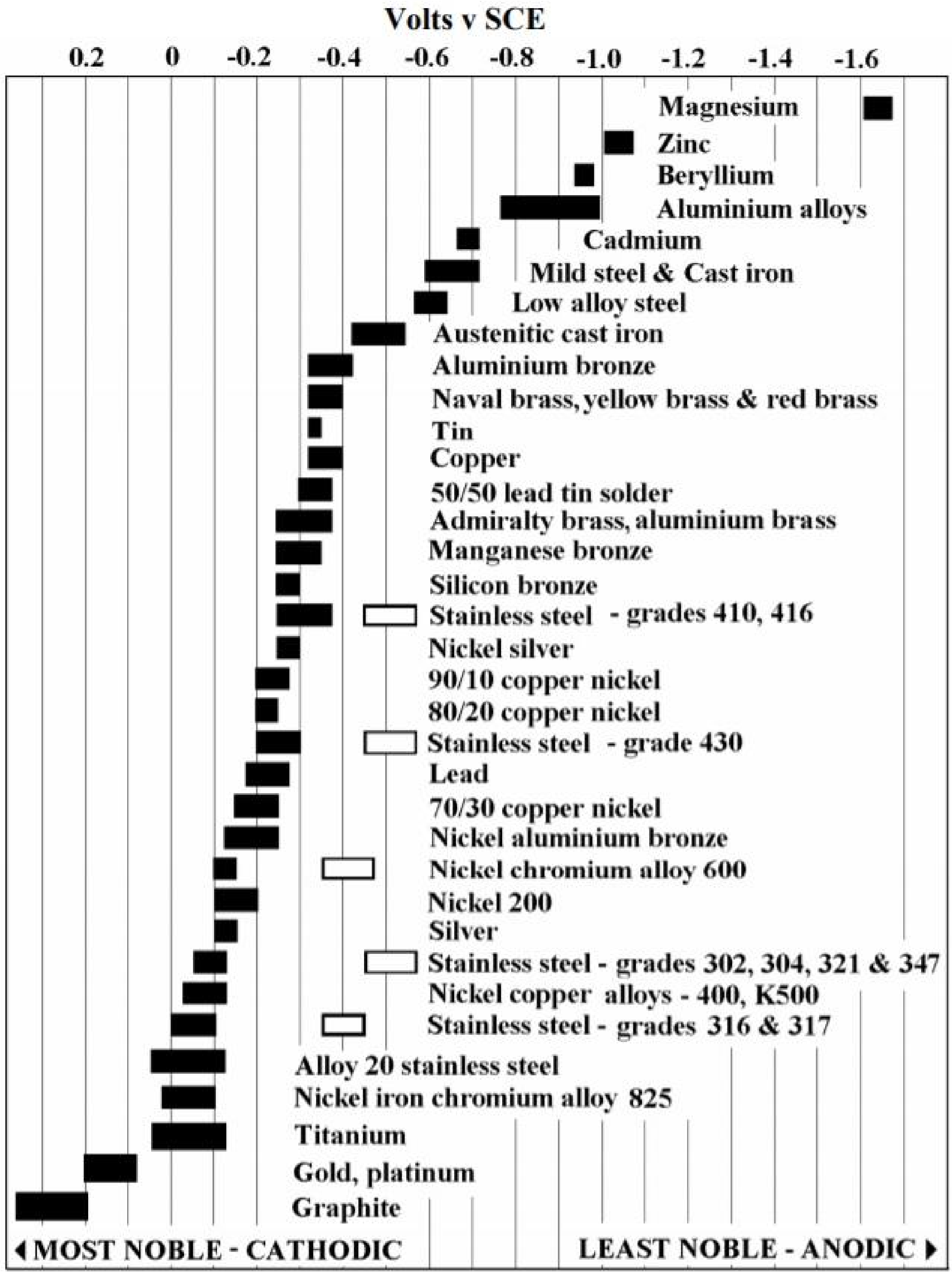


Figure 2-2. Galvanic series noble metals with saturated calomel electrode (SCE) (Tugsataydin, 2017)

The aluminum hydration reaction draws attention as it can produce hydrogen without greenhouse gas emissions and without requiring separate energy compared to the existing green hydrogen production process. Hydrogen produced through aluminum hydration showed an energy requirement of 2% and CO_2 emission of 4% compared to conventional hydrogen production methods when various processes, such as residue treatment, were considered in the life cycle assessment (Hiraki et al., 2005).

Recently, a method of adding a liquid metal such as gallium to an aluminum hydration reaction has been proposed. Gallium has a much freer atomic arrangement than aluminum, so it penetrates aluminum, which is a regular atomic arrangement. As a result, it collapses the regular atomic structure of aluminum and cracks the surface. So gallium reduces aluminum's mechanical strength and activates aluminum's surface, making hydrogen production using water easier. When 15% of a liquid metal eutectic (Ga_{60}-In_{25}-Sn_{10}-Zn_5) was combined with 60 μm aluminum particles, the aluminum hydration reaction showed a fast reaction and 97.5% hydrogen yield (Jayaraman et al., 2015). In addition, when the liquid metal eutectic ($Ga_{68.5}$-$In_{7.875}$-$Sn_{16.38}$-$Bi_{7.245}$) was used, the aluminum hydration reaction effect was better than the other liquid metal eutectic ($Ga_{75.5.5}$-$In_{24.5}$, $Ga_{68.5}$-$In_{13.734}$-$Sn_{17.766}$). An aluminum hydration reaction with a gallium eutectic, when carried out with an aluminum plate of 3 g, shows an output of 0.73 W, and the result shows the possibility of an aluminum hydration reaction as a hydrogen source in PEMFC (Xu et al., 2020).

2.2 Hydrogen storage technologies

Hydrogen has the highest energy density of any fuel because it is the lightest element on the periodic table. However, hydrogen is difficult to store because it has a very low volumetric energy density. There are three main ways to store hydrogen. Hydrogen can be compressed, liquified, or chemically combined. A significant problem in the hydrogen industry is transportation and storage. Hydrogen is produced in gaseous form and must be stored under high pressure or liquefied at low temperatures and high pressure. These processes have many problems because additional energy must be supplied to create a low-temperature and high-pressure state. Another method is to store hydrogen by chemical bonding. In chemical bonding, there are main methods to store hydrogen in liquid organic hydrogen carriers (LOHC) or ammonia.

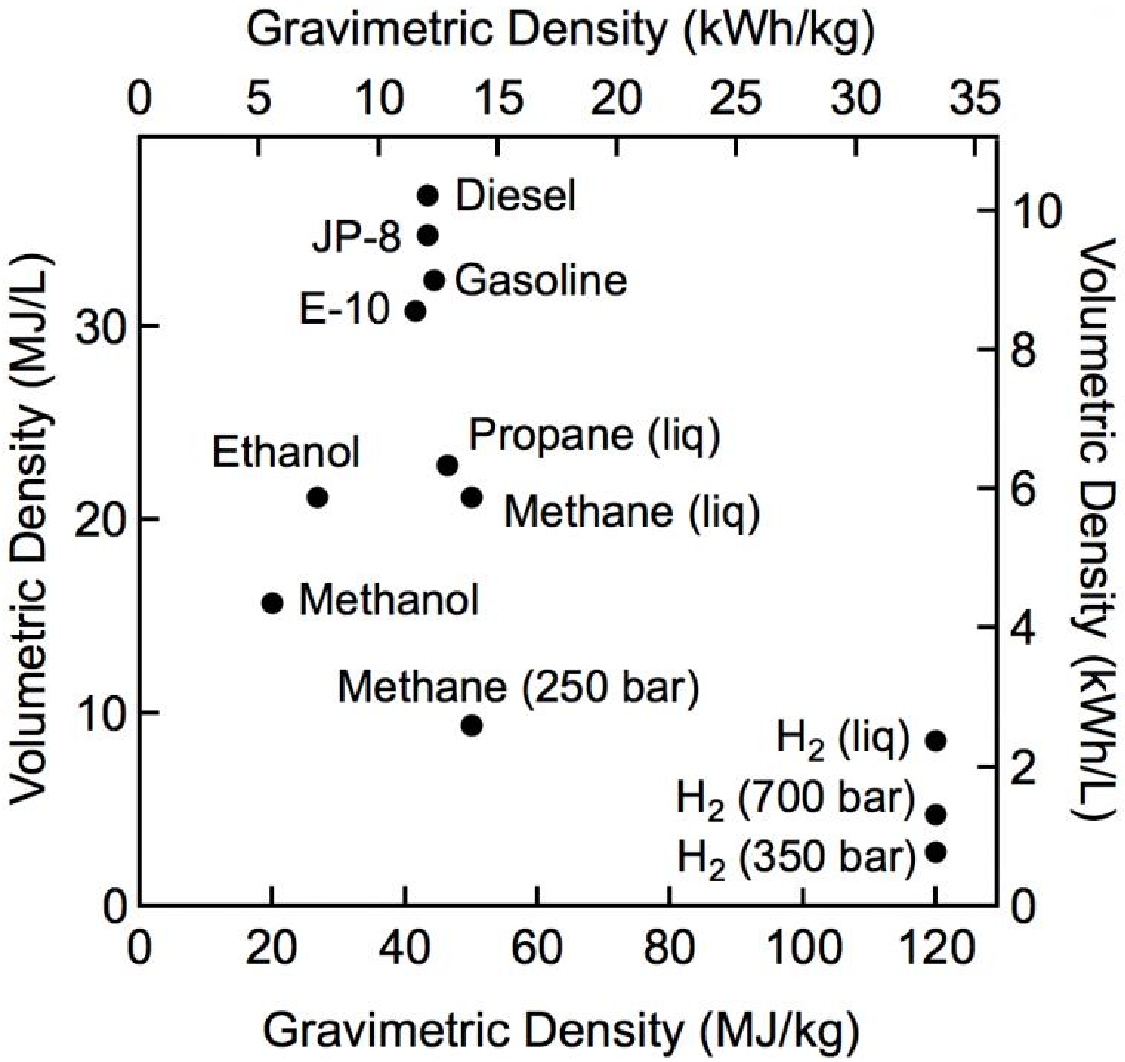


Figure 2-3. Comparison of specific energy (energy per mass or gravimetric density) and energy density (energy per volume or volumetric density) for several fuels based on lower heating values (DOE, n.d.)

2.2.1 Compressed hydrogen

Currently, the most commonly used hydrogen storage technology is a technology that stores hydrogen by compressing it into a high-pressure tank. The high-pressure hydrogen tank is a method of putting hydrogen into a tank made of non-metal liners and carbon fiber composite materials. It requires high technical skills with an internal pressure of about 700 bar (Johnson et al., 2017). Most hydrogen cars currently in production use this method to store hydrogen. However, there is a problem it takes much energy to compress the gas at high pressure, and it is not easy to develop a small container that is lightweight and durable.

2.2.2 Liquid hydrogen

Liquefied hydrogen is made under low temperatures and high pressure and stored in tanks. By converting hydrogen into a liquid, the energy density increases by a factor of 800, significantly increasing the efficiency as a fuel. Pressure is also essential in liquefying hydrogen, but for gas to turn into liquid, it must go through the critical temperature required for each material. In the case of hydrogen, the critical temperature reaches -240 ℃, which makes it difficult. Generally, when liquefying hydrogen, a method of increasing the pressure and then lowering the temperature to -253 ℃ through a heat exchanger is mainly used (Kim et al., 2018).

2.2.3 Chemically combined hydrogen

Chemically combined hydrogen is a method that is chemically combined and used through catalyst or pyrolysis when necessary. There are ways to use liquid organic hydrogen carriers (LOHC) and ammonia. LOHC is a chemical hydrogen storage method that stores hydrogen in liquid organic material. When hydrogen is absorbed or released, carbon dioxide is not emitted and is stable at room temperature. There are representative LOHCs, such as Methylcyclohexane or Dibenyzltoluene, which require a certain amount of high temperature and high-pressure conditions when it absorbs or releases hydrogen (Sekine et al., 2021).

Next, there is a method of storing and using hydrogen in the form of ammonia. Ammonia has a light feature and a boiling point of -33.4 ℃, making it relatively easy to transport in a liquefied state. In addition, the flame range is narrower than conventional hydrogen, so it is safe and greatly advantageous for storage and transportation (Kim et al., 2020).

2.3 Hydrogen utilization technologies (Fuel cells)

Hydrogen energy is drawing attention as an alternative to solving this problem as renewable energy development becomes active due to climate change caused by fossil fuel depletion and excessive greenhouse gas emissions (IEA, 2019). Hydrogen occupies 75% of the materials in the universe, and only water is generated as a by-product during combustion, so it is highly valued from an environmental and energy perspective (Kim et al., 2018; Staffell et al., 2019). A fuel cell that converts the chemical energy of hydrogen into electrical energy using a continuous electrochemical reaction of hydrogen is a representative technology that utilizes hydrogen as an energy source. Depending on the type of electrolyte, the fuel cell is an alkaline fuel cell (AFC), a proton exchange membrane fuel cell (PEMFC), a direct methanol fuel cell (DMFC), and a phosphoric acid fuel cell. (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), etc. (Abdelkareem et al., 2019; Lee et al., 2020).

Table 2-1. Types of fuel cells

Fuel cell type	PAFC	PEMFC	AFC	MCFC	SOFC
Full name	Phosphoric acid fuel cell	Polymer electrolyte membrane fuel cell; Proton exchange membrane fuel cell	Alkaline fuel cell	Molten carbonate fuel cell	Solid oxide fuel cell
Electrolyte	Liquid H_3PO_4 (Immobilized)	Solid polymer membrane	Liquid KOH (Immobilized)	Liquid molten carbonate (Li_2CO_3/K_2CO_3)	Solid ceramic YSZ or GDC
Charge carrier	H^+	H^+	OH^-	CO_3^{2-}	O^{2-}
Electron acceptor	O_2	O_2	O_2	O_2, CO_2	O_2
Catalyst	Pt	Pt	Pt	Ni	Perovskites / Ni
Fuel	H_2	H_2 (DMFC: CH_3OH)	H_2	H_2, LNG (CH_4)	H_2, LNG (CH_4), CO
Operation temperature (℃)	150~250	60~100	40~120	550~770	800~1000
Efficiency (%)	40~50	40~60	45~60	45~60	50~60
Internal reforming	No	No	No	Yes	Yes

2.3.1 PAFC

A phosphoric acid fuel cell (PAFC) uses liquid phosphoric acid as an electrolyte and a porous carbon electrode containing a platinum catalyst. PAFC is the most mature fuel cell and was first applied for commercial use, and its degradation in electrolytes is relatively less than PEMFC. Also, PAFC can use low concentrations of hydrogen (70~90%) as fuel. Combined heat and power (CHP) generation is more efficient than 85% but less efficient in generating electricity alone (40%~50%) (Ellamla et al., 2015). PAFC are also less powerful than other fuel cells, considering the same weight and volume. PAFC is also expensive. They need a much higher-priced platinum catalyst than other fuel cells, increasing the cost. The electrochemical reactions occurring in PAFC are shown in equations (2.1), (2.2), and (2.3).

$$\text{Anode : } H_{2(g)} \rightarrow 2H^+ + 2e^- \qquad E° = 0.00\ V \quad (2.1)$$

$$\text{Cathode : } ½O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_{(l)} \qquad E° = +1.23\ V \quad (2.2)$$

$$\text{Overall reaction : } H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(l)} \qquad E_{cell} = +1.23\ V \quad (2.3)$$

2.3.2 AFC

Alkaline fuel cell (AFC) is one of the first fuel cell technologies developed and was widely used in the US space program to produce electricity and water in spacecraft in the 1960s. It uses an aqueous potassium hydroxide solution as an electrolyte, and various inexpensive materials (Ni, Ag, etc.) can be used. It has an advantage in terms of price, but AFC has the feature that it can be easily poisoned by carbon dioxide, and even a small amount of carbon dioxide in the air can affect cell performance. Carbonate has a characteristic of being precipitated due to its low solubility, and it blocks the pores of the porous electrode and causes electrode degradation. It can be a significant impact on durability. Since the development of low-temperature operating

PEMFC, it has been rarely used for anything other than spacecraft. The electrochemical reactions occurring in AFC are shown in equations (2.4), (2.5), and (2.6).

$$\text{Anode : } H_{2(g)} + 2OH^- \rightarrow 2H_2O_{(l)} + 2e^- \qquad E° = +0.83\ V \tag{2.4}$$

$$\text{Cathode : } O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^- \qquad E° = +0.40\ V \tag{2.5}$$

$$\text{Overall reaction : } H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad E_{cell} = +1.23\ V \tag{2.6}$$

2.3.3 MCFC

Molten carbonate fuel cell (MCFC) is currently being developed for natural gas and coal-based power plants for the electric utility, industrial and military applications. MCFC is a fuel cell that uses an electrolyte composed of a molten carbonate mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide matrix. MCFC can reach efficiencies approaching 45% to 60%. Also, CHP generation can have 85% efficient. Because it operates at a high temperature of 550 to 770 ℃, the activation energy required for the reduction-oxidation (REDOX) reaction is provided through heat, and non-precious metal catalysts can be used. Internal reforming can reduce the cost of the overall system. However, operating at high temperatures accelerates the deterioration of the electrolyte and components, reducing the battery's life. The electrochemical reactions occurring in AFC are shown in equations (2.7), (2.8), and (2.9).

$$\text{Anode : } H_{2(g)} + CO_3^{2-} \rightarrow H_2O_{(l)} + CO_{2(g)} + 2e^- \tag{2.7}$$

$$\text{Cathode : } O_{2(g)} + 2CO_{2(g)} + 4e^- \rightarrow 2CO_3^{2-} \tag{2.8}$$

$$\text{Overall reaction : } H_{2(g)} + \tfrac{1}{2}O_{2(g)} + CO_{2(g,\ cathode)} \rightarrow H_2O_{(l)} + CO_{2(g,\ anode)} \tag{2.9}$$

2.3.4 SOFC

Solid oxide fuel cell (SOFC) uses solid ceramic YSZ or GDC as electrolytes. SOFC has an electrical efficiency of 60% and an efficiency of 85% when CHP power generation is additionally generated. SOFC operates at a very high temperature of 1000 ℃ and has an economic advantage because various fuels like MCFC can be used through internal reforming. Therefore, there is no need for a precious metal catalyst. However, materials are subject to strict durability requirements due to the high operating temperature. Therefore, developing low-cost materials with high durability at cell operating temperatures is a critical technical challenge facing this technology. The possibility of developing SOFC at low temperatures is currently being sought to solve this problem. The electrochemical reactions occurring in SOFC are shown in equations (2.10), (2.11), and (2.12).

$$\text{Anode : } H_{2(g)} + O^{2-} \rightarrow H_2O_{(l)} + 2e^- \qquad (2.10)$$

$$\text{Cathode : } O_{2(g)} + 4e^- \rightarrow 2O^{2-} \qquad (2.11)$$

$$\text{Overall reaction : } H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad (2.12)$$

2.3.5 PEMFC

In this study, hydrogen generated through the aluminum hydration reaction was directly supplied into the polymer electrolyte membrane fuel cell (PEMFC) for evaluation. PEMFC mainly uses a proton conductive polymer electrolyte membrane using a perfluorinated sulfonic acid polymer. PEMFC is in the form of an anode and cathode attached to a porous carbon support material on both sides of the membrane, and the structure is shown in Figure 2-4.

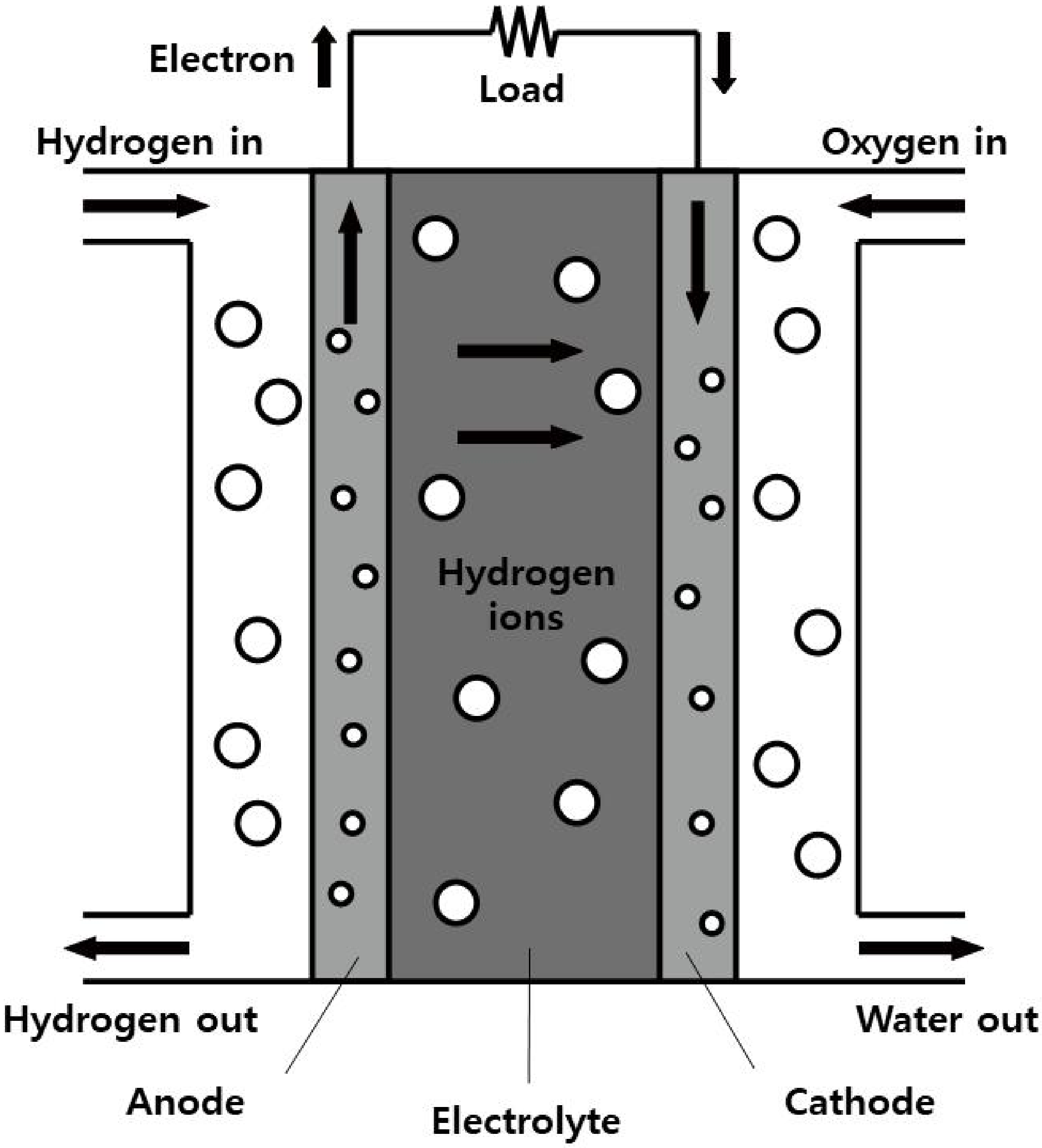


Figure 2-4. Schematic of polymer electrolyte membrane fuel cell (PEMFC)

At the anode, oxidation of hydrogen occurs. Moreover, the reduction of oxygen occurs at the anode. In this process, as electrons move, an electric current is generated. Each half-reaction at the cathode and the anode and the overall reaction equations are as follows.

Anode : $H_{2(g)} \rightarrow 2H^+ + 2e^-$ $E° = 0\ V$ (2.13)

Cathode : $\frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_{(l)}$ $E° = +\ 1.23\ V$ (2.14)

Overall reaction : $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ $E_{cell} = +1.23\ V$ (2.15)

PEMFC operates at a relatively low temperature (60~100 ℃) compared to other fuel cells and has a high power density (500~2500 mW/cm^2) due to its small weight and volume, so it is mainly used as a power source in the transportation field and a moving power source.

3. Methodology

3.1 Preparation and pretreatment of waste aluminum

The aluminum used in this study are UBCs (used beverage cans, A3104), de-coated Al can granules (A3104, A5182), construction aluminum materials (A6063), yogurt lids (A8011), and high-purity aluminum with a purity of 99.99%. Each aluminum was molded to the same size for the same test conditions and treated with the same weight.

De-coated Al can granules produced at the Suncheon Yulcheon plant of DS LIQUID, a recycling company specializing in recycling, were used for the pre-treated aluminum cans. It is a granules-type waste aluminum made by removing paint and polymer coated on the outside using a rotary kiln and finely crushing it with a crusher.

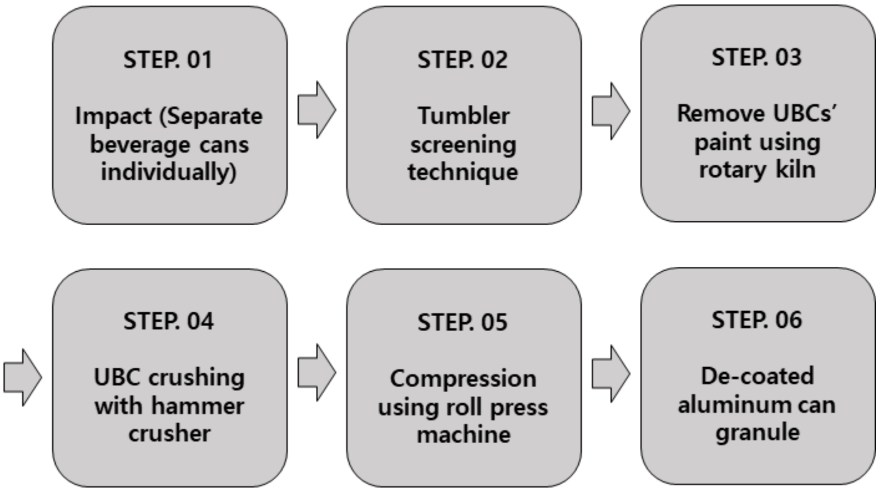


Figure 3-1. De-coated Al can granules production process (DS LIQUID, n.d.)

Table 3-1. Chemical composition of commercial aluminum alloy in this experiment

Al	Si	Fe	Cu	Mg	Mn	Zn	Ti	Pb	Ca	Na	Cr	Other	Al (Min, %)
	Chemical composition (Max, w/w%)												
A3014	0.3	0.5	0.25	1.5	1	0.2	0.03	0.001	0.001	0.005	0.03	-	>96.5
A5182	0.15	0.3	0.1	5	0.5	0.05	0.03	0.001	0.001	0.005	0.03	-	>95
A6063	0.6	0.35	0.1	0.9	0.1	0.1	0.1	0.05	0.05	0.05	1	-	>97.5
A8011	0.9	1	0.1	0.05	0.12	0.1	0.08	0.05	0.05	0.05	0.05	-	>97.3

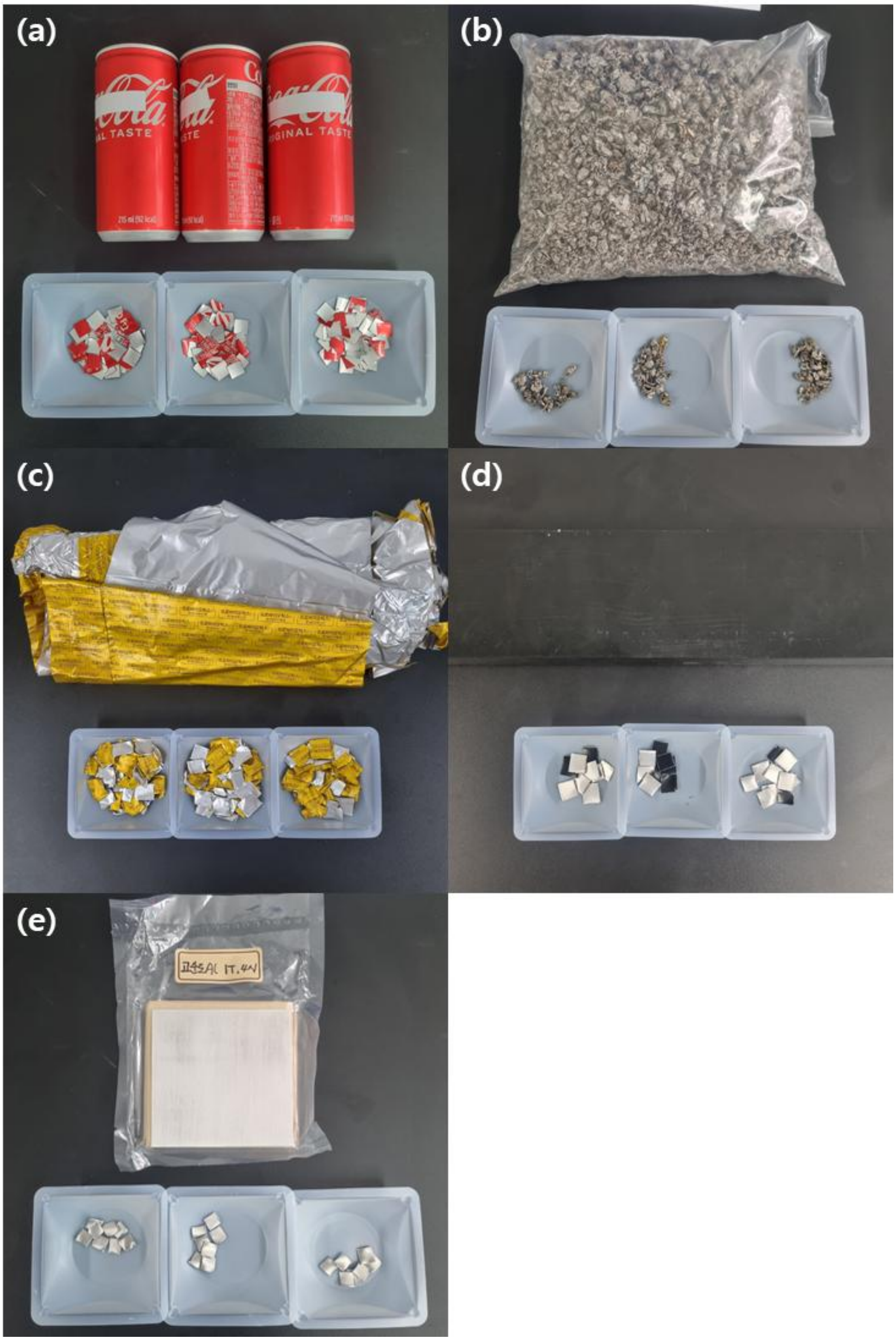


Figure 3-2. Aluminum samples used in aluminum hydration reaction, (a) Used beverage cans (A3104), (b) De-coated Al can granules (A3104, A5182), (c) Construction Al materials (A6063), (d) Yogurt lids (A8011), (e) High-purity Al (99.99%)

Table 3-2. Chemical composition of yogurt lids

Component	Composition (w/w %)
Cu	0.13040
Mn	0.00214
Al	74.08820
Mg	0.00178
Plastic	25.80000

3.2 Waste aluminum hydration

In the aluminum hydration reaction, when an alkaline solution is added, such as NaOH, it is not consumed and acts like a catalyst. At the same time, aluminum has a corrosion reaction, and water produces hydrogen as a reduction reaction occurs. If the aluminum hydration reaction is calculated stoichiometrically, it can make 1.35 L/g-H_2 theoretically under 1 atm and 298 K. The aluminum hydration reaction equations are as follows.

$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2 \tag{3.1}$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \tag{3.2}$$

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{3.3}$$

The reaction tank for the aluminum hydration reaction was designed to measure the reaction immediately by attaching a syringe to the Buchner flask. The experiment was conducted with different types of aluminum. The size, weight, temperature, and amount of NaOH solution were adjusted to the same conditions as possible, and the experiment was conducted with different molar concentrations of NaOH solution.

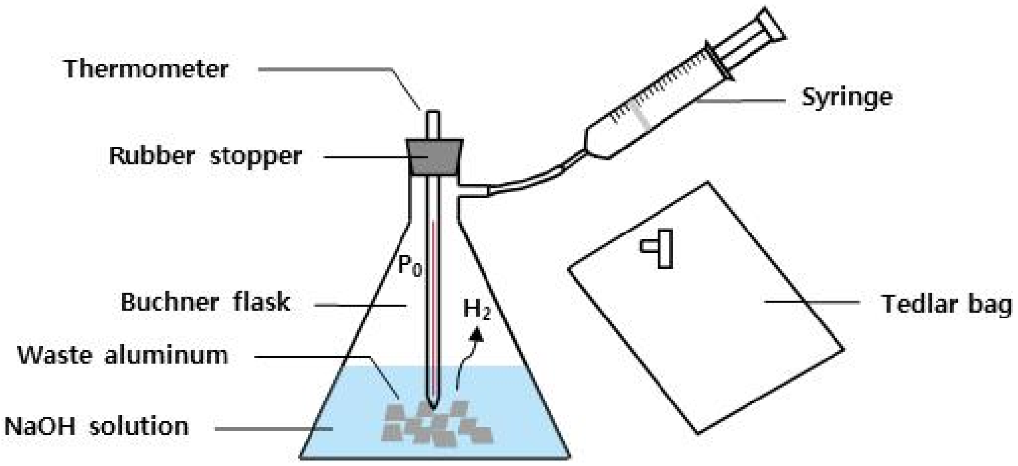


Figure 3-3. Experimental scheme for aluminum hydration reaction

Table 3-3. Experiment conditions of aluminum hydration reaction

Aluminum type	Used beverage cans (A3104)	De-coated Al can granules (A3104, A5182)	Aluminum for construction materials (A6063)	Yogurt lids (A8011)	High-purity Al (99.99%)
Weight (g)	5	5	5	5	5
Size	1cm x 1cm x 0.13mm	8∅ ~ 23∅ (Irregular)	1cm x 1cm x 1mm	1cm x 1cm x 0.05mm	1cm x 1cm x 0.1cm
Temperature (℃)	25	25	25	25	25
Amount of NaOH solution (ml)	200	200	200	200	200
Molar concentration of NaOH solution	1 / 3 / 5	1 / 3 / 5	1 / 3 / 5	1 / 3 / 5	1 / 3 / 5

3.3 Quantitative hydrogen detection

The hydrogen gas produced by the aluminum hydration reaction was directly collected through a tedlar bag, and gases with a hydrogen content of 99.999%, 80%, 50%, and 25% were manufactured to prepare a calibration curve (Figure 3-5). Hydrogen was analyzed by using gas chromatography (GC; 6890N, Agilent Technology, USA) equipped with a micropacked column (ShinCarbon ST column, 100/120 2m 1mmID 1/16"OD, Restek, USA) and a thermal conductivity detector (TCD). The GC was operated with conditions of the injector (100 ℃), oven (40 ℃), and detector (110 ℃).

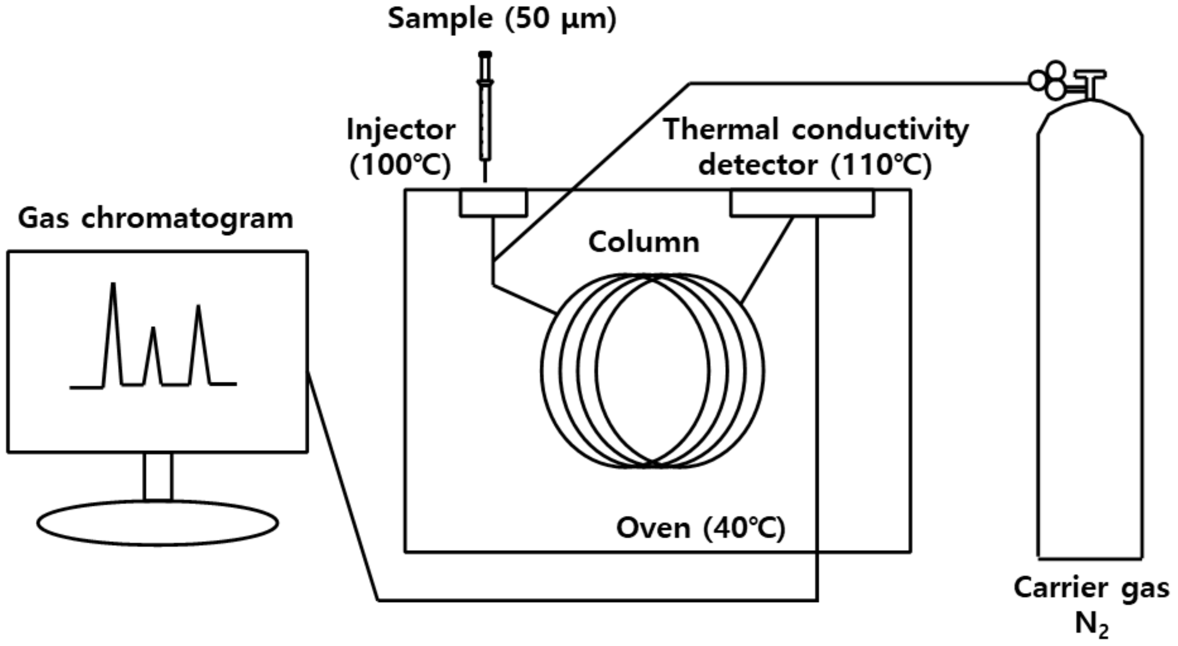
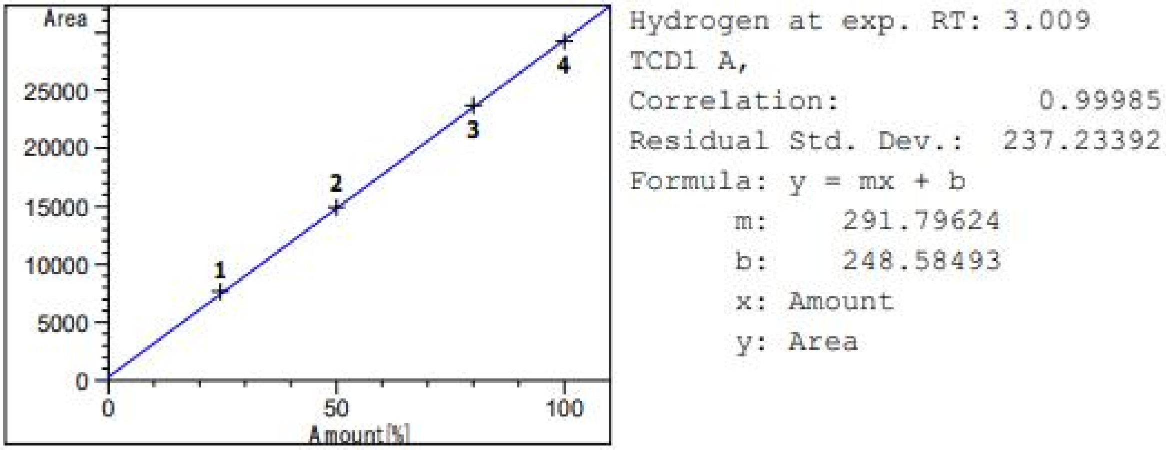


Figure 3-4. Experimental scheme for gas chromatography



```
Hydrogen at exp. RT: 3.009
TCD1 A,
Correlation:              0.99985
Residual Std. Dev.:   237.23392
Formula: y = mx + b
        m:     291.79624
        b:     248.58493
        x: Amount
        y: Area
```

Figure 3-5. Calibration curve for hydrogen concentration detection

3.4 PEMFC performance analysis

The fuel cell performance was measured using a unit cell (PEMFC, Nara cell tech) with an electrode area of 25 cm^2 and a 7-layer MEA (VMEA-SERIES, Horizon). In general, a warm-up is performed before measuring the performance of the battery to ensure the equilibrium of the fuel cell system. Stabilizing the performance of the unit cell repeated the voltage cycle activation technique 30 times in the 0.7 V-0.5 V range. The performance analysis was performed by fixing the cell and gas injection temperature to 70 ℃. The hydrogen and air flow rates were supplied with a fixed flow rate of 348 and 870 ml/min, respectively, using a mass flow controller (MFC, Alicat). A bubbler-type humidifier was used to control the relative humidity of the fuel to 100%.

To analyze the characteristics of MEA after operating the fuel cell, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured with a potentiostat (V43219, Ivium). After each experiment, the cell was purged with 200 sccm (standard cubic centimeters per minute) of the humidified nitrogen for 30 min to remove impurities that may remain inside the cell completely.

In the cyclic voltammetry (CV) analysis, hydrogen (40 sccm) and nitrogen (200 sccm) were supplied to an anode, and a cathode, respectively, and a current was measured with a scan rate of 30 mV/s at a cell temperature of 70 ℃ and relative humidity of 100%.

Impedance measurement was performed with 70 ℃ cell temperature, 100% relative humidity, 1 A DC, 100 mA AC amplitude, and 10,000 to 0.001 Hz, supplying hydrogen (93 sccm) and air (296 sccm) to anode and cathode, respectively.

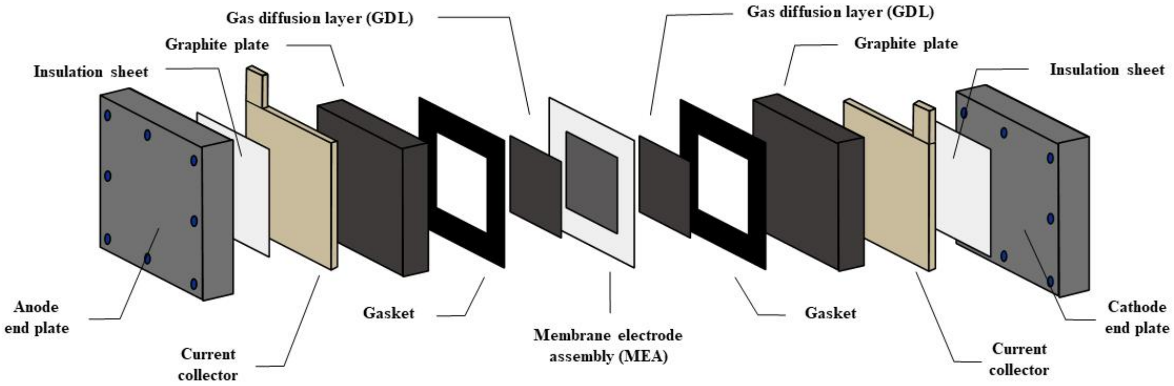


Figure 3-6. Unit cell structure of polymer electrolyte membrane fuel cell

Table 3-4. Experiment conditions of polymer electrolyte membrane fuel cell

Anode	Size	25 cm^2 (5x5)
	Material	Pt/C
	Operation temperature	70 ℃
	Relative humidity(%)	100
Cathode	Size	25 cm^2 (5x5)
	Material	Pt/C
	Operation temperature	70 ℃
	Relative humidity(%)	100

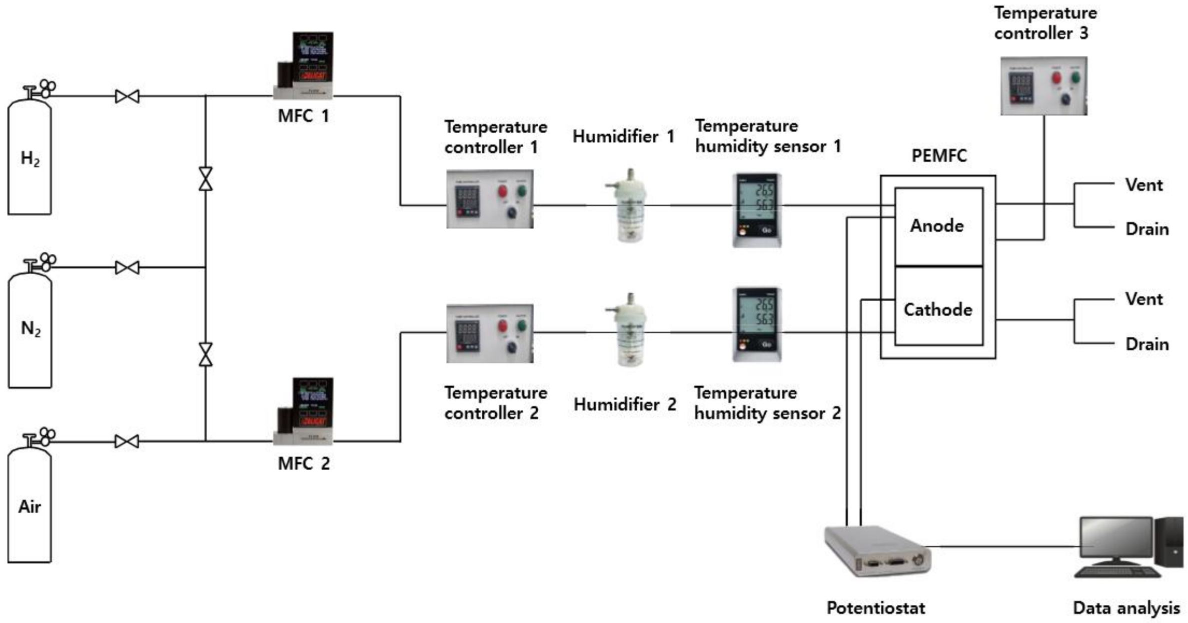


Figure 3-7. Experimental scheme for electrochemical analysis

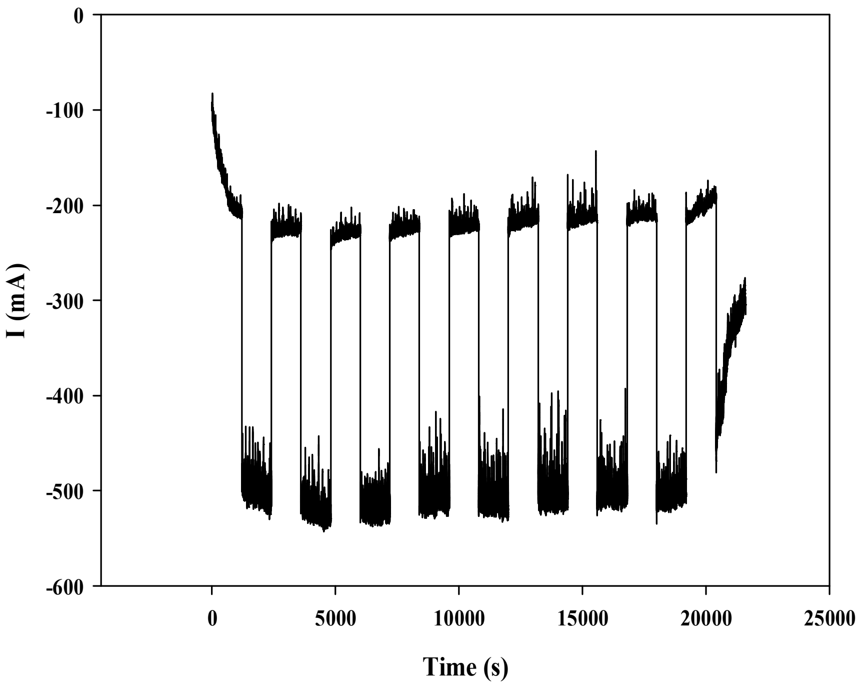


Figure 3-8. Voltage cycle activation technique (0.7 V to 0.5 V)

4. Results and discussion

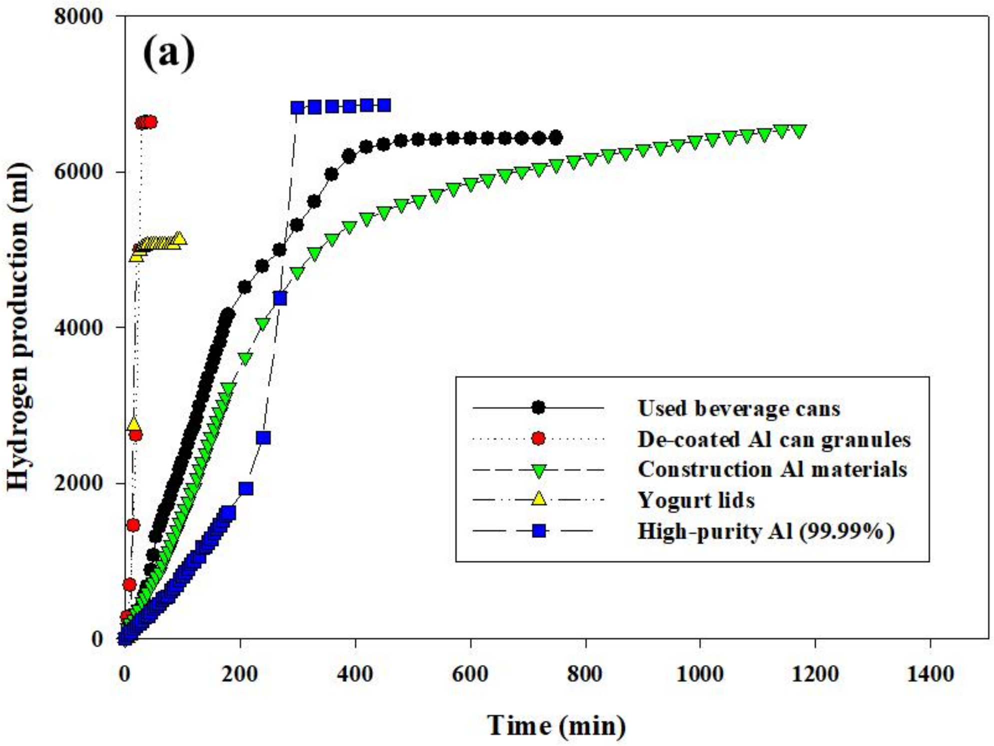
4.1 Waste aluminum hydration

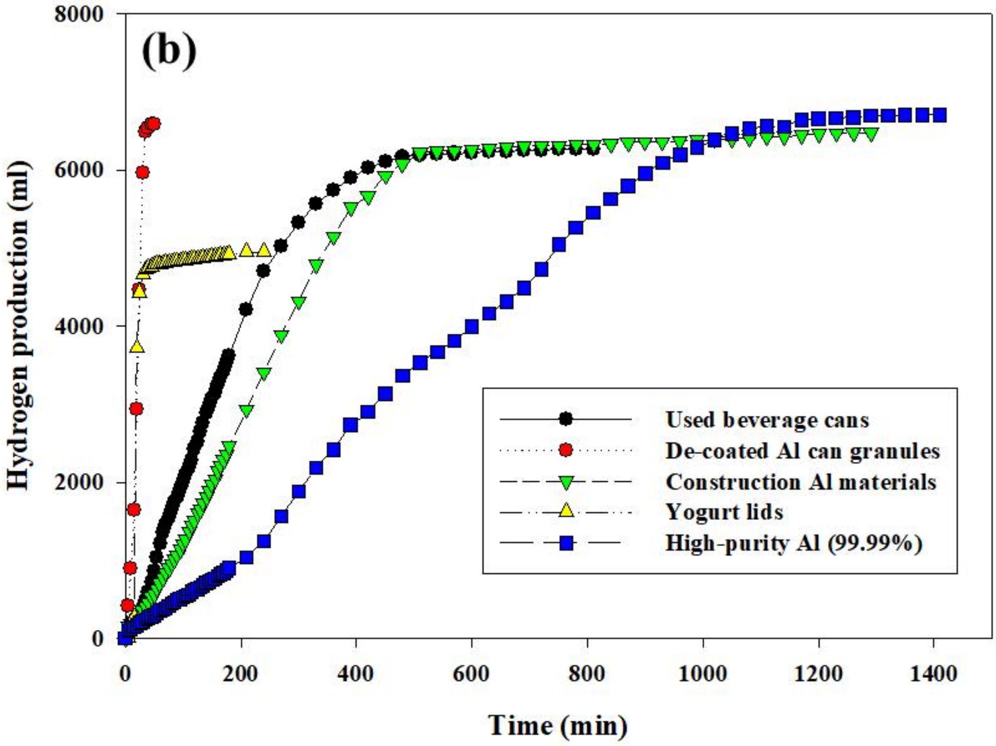
The waste aluminum hydration reaction was performed with five types of aluminum samples: UBCs (used beverage cans, A3104), de-coated Al can granules (A3104, A5182), construction aluminum materials (A6063), yogurt lids (A8011), and high-purity aluminum with a purity of 99.99%.

4.1.1 Hydrogen production

The waste aluminum hydration reaction was performed with 5 g of waste aluminum and 200 ml of 1, 3, and 5 M NaOH aqueous solution. The hydrogen production was 6435, 6630, 6540, 5124, and 6855 mL, respectively, when 5g of UBCs, de-coated Al can granules, construction Al materials, yogurt lids, and high-purity aluminum were added with 5 M NaOH solution. In the 3 M NaOH solution, hydrogen was produced in 6270, 6580, 6480, 4950, and 6710 mL, respectively. In the 1 M NaOH solution, the reaction was very slow compared to 3 M and 5 M concentrations, and the temperature was low, so $Al(OH)_3$ became a solid state during the reaction and did not react for a long time. In this experiment, considering these points, hydrogen generation was measured for 120 minutes, and hydrogen was produced in 885, 5430, 774, 4015, and 362 mL, respectively.

According to a report by Rosenband et al. (2010), 1240 mL of hydrogen is generated stoichiometrically from 1g of aluminum in a standard state (1atm, 273K), and almost 100% hydrogen production yield is shown under appropriate operating conditions. The amount of hydrogen produced was evaluated by integrating the actual aluminum content of the gases generated through the aluminum hydration reaction and the concentration of hydrogen released through the aluminum hydration reaction. In 3 M and 5 M NaOH solutions, the UBCs were 87.88% and 90.19%. 99.12% and 99.87% hydrogen was generated from de-coated Al can granules, 98.05% and 98.96% hydrogen from construction aluminum materials, 88.68% and 91.79% hydrogen from yogurt lids, and 96.06% and 98.13% hydrogen from high-purity Al, respectively. In the case of de-coated can granules, construction aluminum materials, and high-purity aluminum, the theoretical hydrogen production was almost the same as the actual hydrogen production. However, in the case of UBCs and yogurt lids, it has been confirmed that the actual production is about 10% lower than the theoretical production. In composite aluminum coated with a polymer, aluminum is hydrated, and the polymer is hydrolyzed. At this time, it is believed that a large amount of decomposed monomers may have affected the hydration reaction of aluminum.




(b)
Hydrogen production (ml)
8000
6000
4000
2000
0
0
200
400
600
800
1000
1200
1400
Time (min)
Used beverage cans
De-coated Al can granules
Construction Al materials
Yogurt lids
High-purity Al (99.99%)

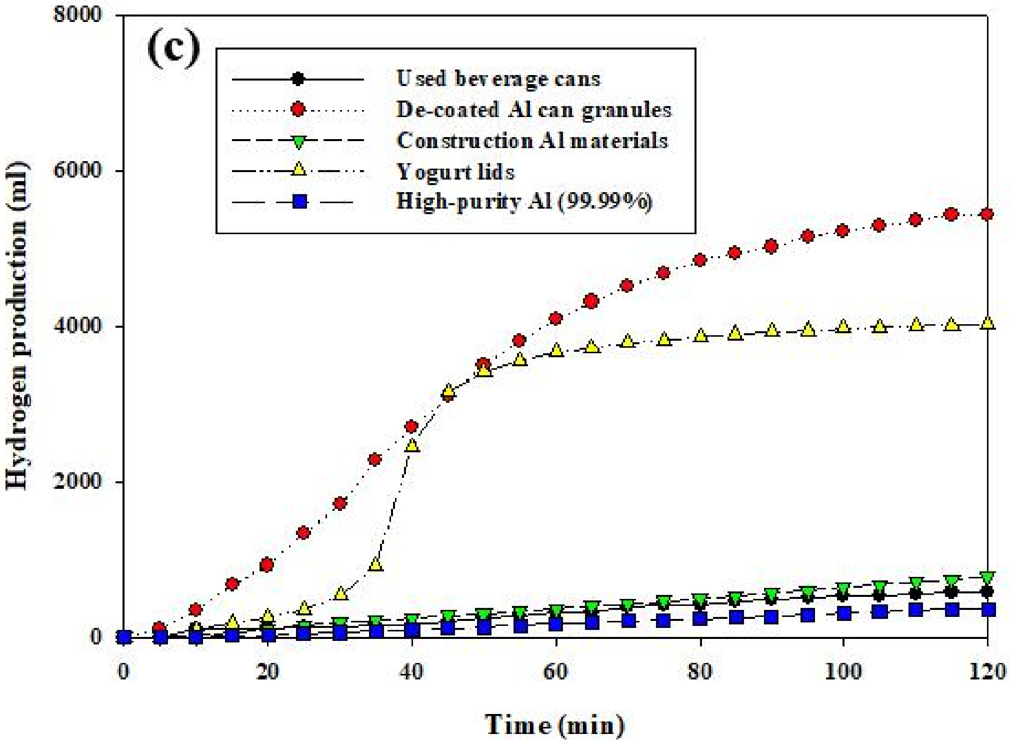


Figure 4-1. Comparison of the amount of hydrogen produced by the waste aluminum hydration reaction according to the molar concentration of NaOH (a) Waste aluminum hydration reaction w/ 5 M NaOH solution, (b) Waste aluminum hydration reaction w/ 3 M NaOH solution, (c) Waste aluminum hydration reaction w/ 1 M NaOH solution (120 mins)

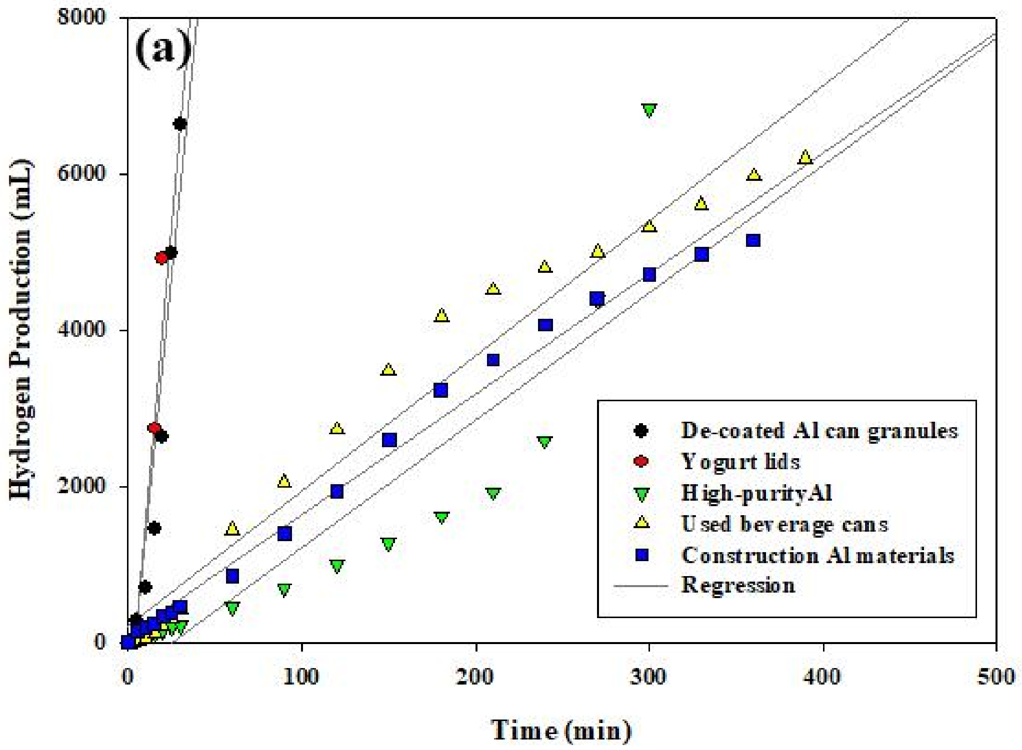
Table 4-1. Comparison of actual and theoretical production of hydrogen generation

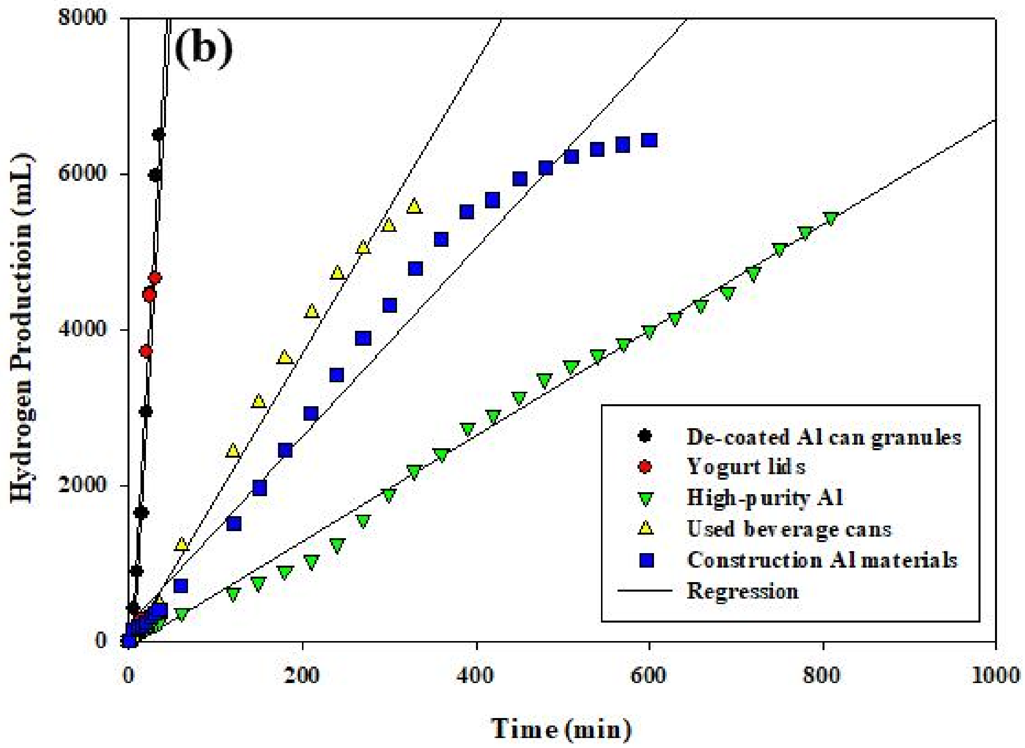
Waste Al type	Al input (g)	Al content (%)	Hydrogen content (%)	Theoretical hydrogen production at 1atm, 298K (ml)	Actual hydrogen production at 1atm, 298K (ml)		Actual/Theoretical (%)	
					3M	5M	3M	5M
Used beverage cans (A3104)	5	<96.50	91.29647	6513.75	5724.29	5874.93	87.88	90.19
De-coated Al can granules (A3104, A5182)	5	<95.00	96.59556	6412.50	6355.99	6404.29	99.12	99.87
Construction aluminum materials (A6063)	5	<97.50	99.58126	6581.25	6452.87	6512.61	98.05	98.96
Yogurt lids (A8011)	5	74.09	89.59089	5001.08	4434.75	4590.64	88.68	91.79
High-purity Al (99.99%)	5	99.99	96.61925	6749.33	6483.15	6623.25	96.06	98.13

4.1.2 Hydrogen production rate

The hydrogen generation rate of the waste aluminum hydration reaction was measured using five types of aluminum samples: UBCs (A3104), de-coated aluminum can granules (A3014, A5182), construction aluminum materials (A6063), yogurt lids (A8011), and high-purity aluminum (99.99%). UBCs produced hydrogen at a rate of 5.092, 18.571, and 17.321 mL/min in the concentrations of 1, 3, and 5 M of the NaOH aqueous solution, respectively. De-coated Al can granules produced hydrogen at a rate of 67.819, 202.890, and 223.114 mL/min. Construction aluminum materials produced hydrogen at a rate of 6.617, 13.650, and 15.455 mL/min, yogurt lids produced hydrogen at a rate of 73.181, 188.107, and 250.980 mL/min, and high-purity Al (99.99%) produced hydrogen at a rate of 3.347, 6.768, and 16.287 mL/min, respectively.

According to Hiraki et al. (2007) and Sim et al. (2009), it has been reported that the hydration reaction of aluminum is affected by the difference and temperature of the galvanic potential. As the NaOH concentration increased, the hydrogen generation rate increased, and the hydrogen generation rate during the reaction tended to increase more rapidly than at the beginning. This phenomenon is believed to have accelerated the hydration reaction due to a gradual increase in temperature through the hydration reaction, and thus the hydrogen generation rate increased. In comparison, untreated UBCs and construction aluminum materials suffered from reaction inhibition due to painting and polymer coating on the surface. High-purity aluminum is considered to have less galvanic corrosion than other waste aluminum. Through this, the interaction between temperature and hydration reaction was confirmed, and it is necessary to derive hydrogen generation optimization conditions by establishing temperature conditions for the hydration reaction.


(a)
Hydrogen Production (mL)
0
2000
4000
6000
8000
Time (min)
0
100
200
300
400
500
● De-coated Al can granules
● Yogurt lids
▼ High-purityAl
△ Used beverage cans
■ Construction Al materials
— Regression


(b)
Hydrogen Productioin (mL)
0
2000
4000
6000
8000
Time (min)
0
200
400
600
800
1000
● De-coated Al can granules
● Yogurt lids
▼ High-purity Al
△ Used beverage cans
■ Construction Al materials
— Regression

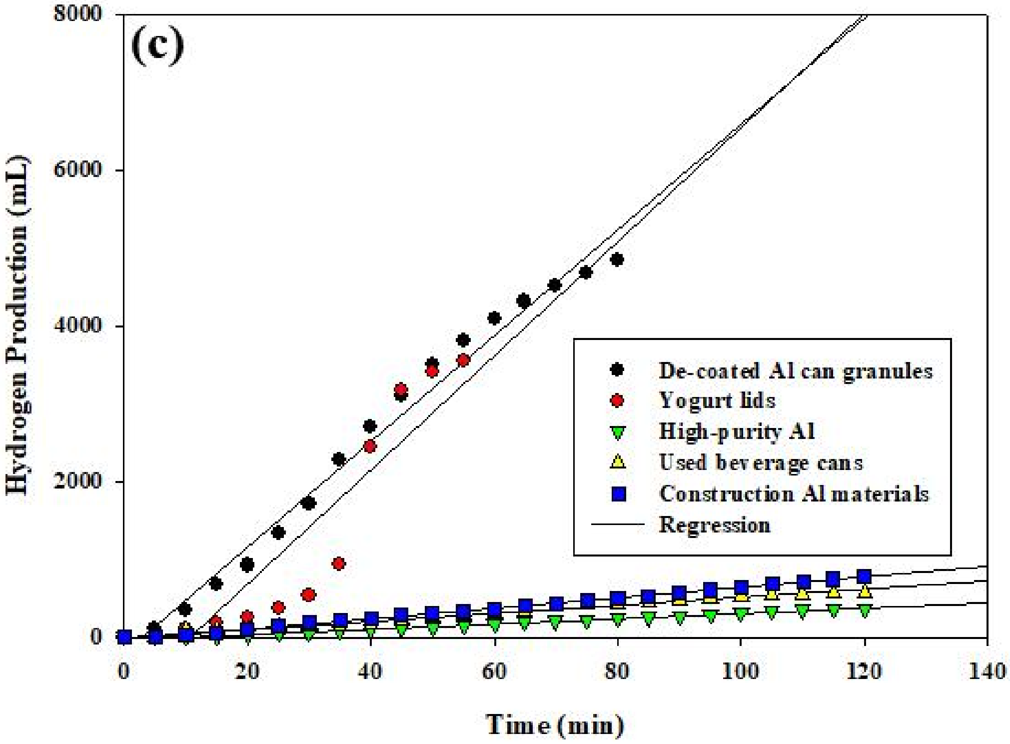


Figure 4-2. Linear regression analysis of hydrogen generation rate according to waste aluminum hydration reaction, (a) Waste aluminum hydration reaction w/ 5 M NaOH solution, (b) Waste aluminum hydration reaction w/ 3 M NaOH solution, (c) Waste aluminum hydration reaction w/ 1 M NaOH solution (120 mins)

Table 4-2. Analysis of hydrogen production rate using waste aluminum composite hydration reaction

Waste Al type	NaOH molar concentration	Hydrogen production rate (mL/min)	R^2
Used beverage cans	1 M	5.092	0.981
	3 M	18.571	0.989
	5 M	17.321	0.964
De-coated Al can granules	1 M	67.819	0.985
	3 M	202.890	0.962
	5 M	223.114	0.900
Construction aluminum materials	1 M	6.617	0.998
	3 M	13.650	0.994
	5 M	15.455	0.989
Yogurt lids	1 M	73.181	0.832
	3 M	188.107	0.825
	5 M	250.980	0.796
High-purity Al (99.99%)	1 M	3.347	0.995
	3 M	6.768	0.994
	5 M	16.287	0.810

4.1.3 Hydrogen composition

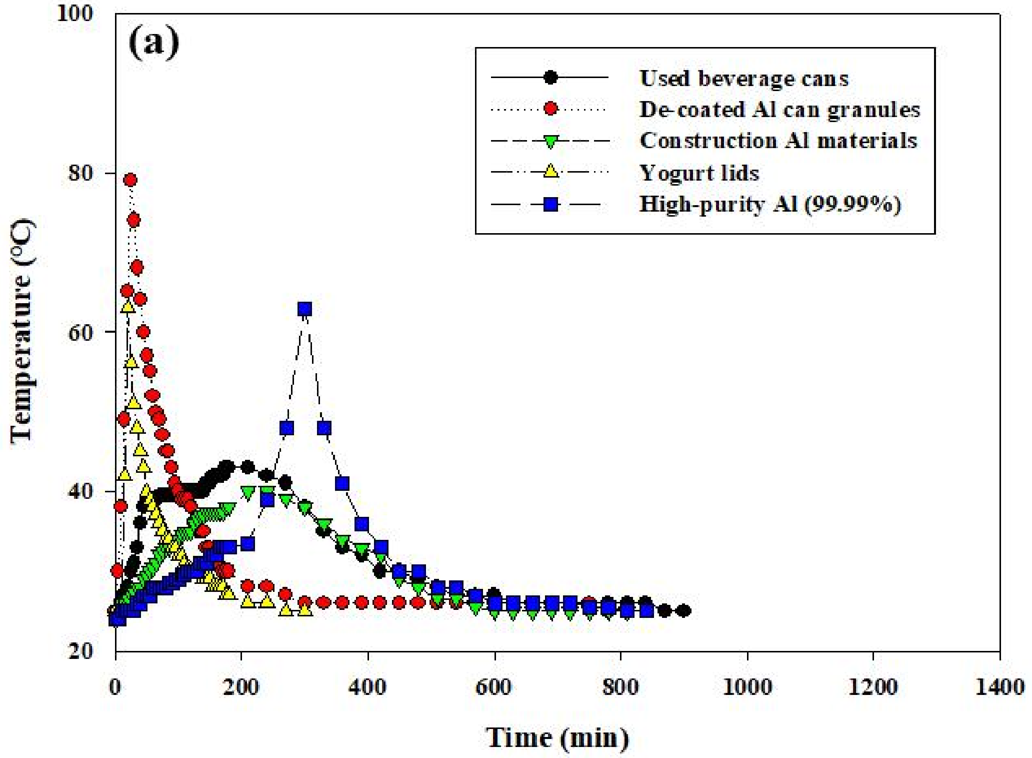
As a result of quantitative analysis of hydrogen gas concentration through the waste aluminum hydration reaction, concentration differences were shown in the following order: construction aluminum materials (A8011), high-purity aluminum (99.99%), de-coated Al can granules (A3104, A5182), UBCs (A3104), and yogurt lids (A8011). The hydrogen generated from construction aluminum materials (A8011) showed a very high hydrogen gas concentration of over 99% (Table 4-3).

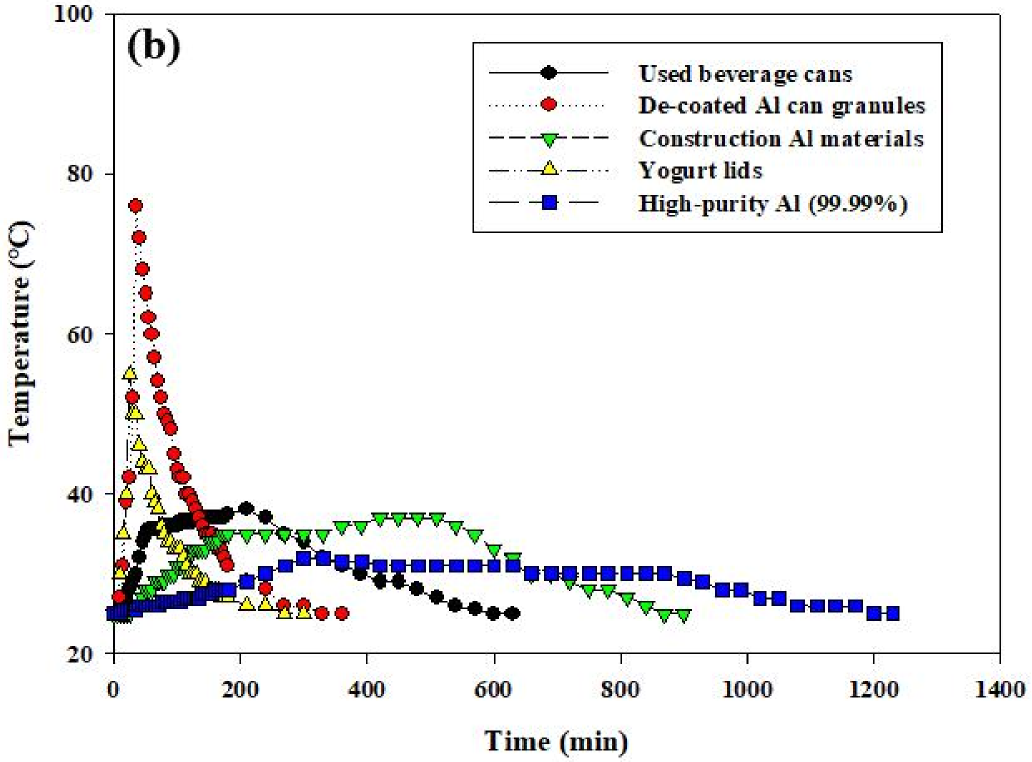
Table 4-3. Composition of hydrogen from waste aluminum composite hydration reaction

Waste Al type	Used beverage cans (A3104)	De-coated Al can granules (A3104, A5182)	Construction aluminum materials (A6063)	Yogurt lids (A8011)	High-purity Al (99.99%)
Hydrogen concentration (%)	91.29647	96.59556	99.58126	89.59089	96.61925

4.1.4 Changes in temperature

In the temperature change through waste aluminum hydration reaction, the temperature of each reactor was measured using UBCs (A3014), de-coated Al can granules (A3104, A5182), construction aluminum materials (A6063), yogurt lids and high-purity aluminum (99.99%). 3 M and 5 M aqueous NaOH solutions were measured until the reaction was completed, and 1 M aqueous NaOH solution was measured for 120 minutes because of its solidification. In the 5 M NaOH solution, the temperature rose to 43, 79, 40, 63, and 63 ℃, respectively. In the 3 M NaOH solution, the temperature rose to 76, 37, 55, and 32 ℃, and in the 1 M NaOH solution, it rose to 28, 51, 29, 60, and 25 ℃ for 120 minutes.


(a)
Temperature (℃)
Time (min)
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
Used beverage cans
De-coated Al can granules
Construction Al materials
Yogurt lids
High-purity Al (99.99%)


(b)
Temperature (℃)
Time (min)
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
Used beverage cans
De-coated Al can granules
Construction Al materials
Yogurt lids
High-purity Al (99.99%)

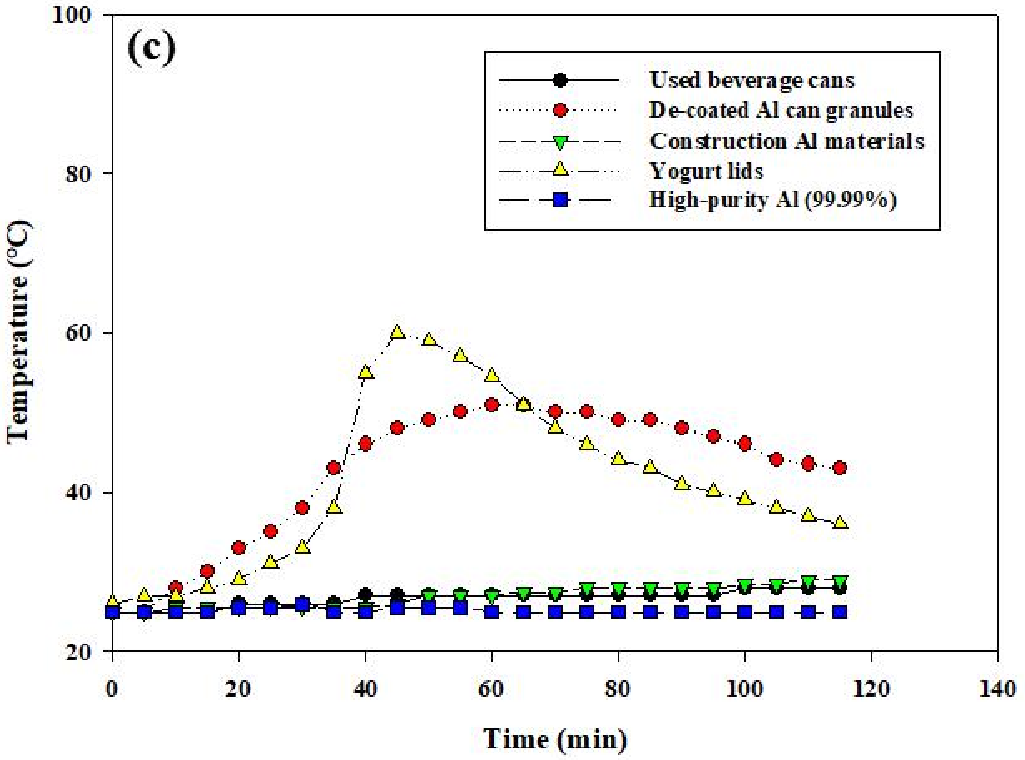


Figure 4-3. Temperature changes in waste aluminum hydration reaction, (a) Waste aluminum hydration reaction w/ 5 M NaOH solution, (b) Waste aluminum hydration reaction w/ 3 M NaOH solution, (c) Waste aluminum hydration reaction w/ 1 M NaOH solution (120 mins)

Table 4-4. Waste aluminum hydration reaction results based on different NaOH molar concentration

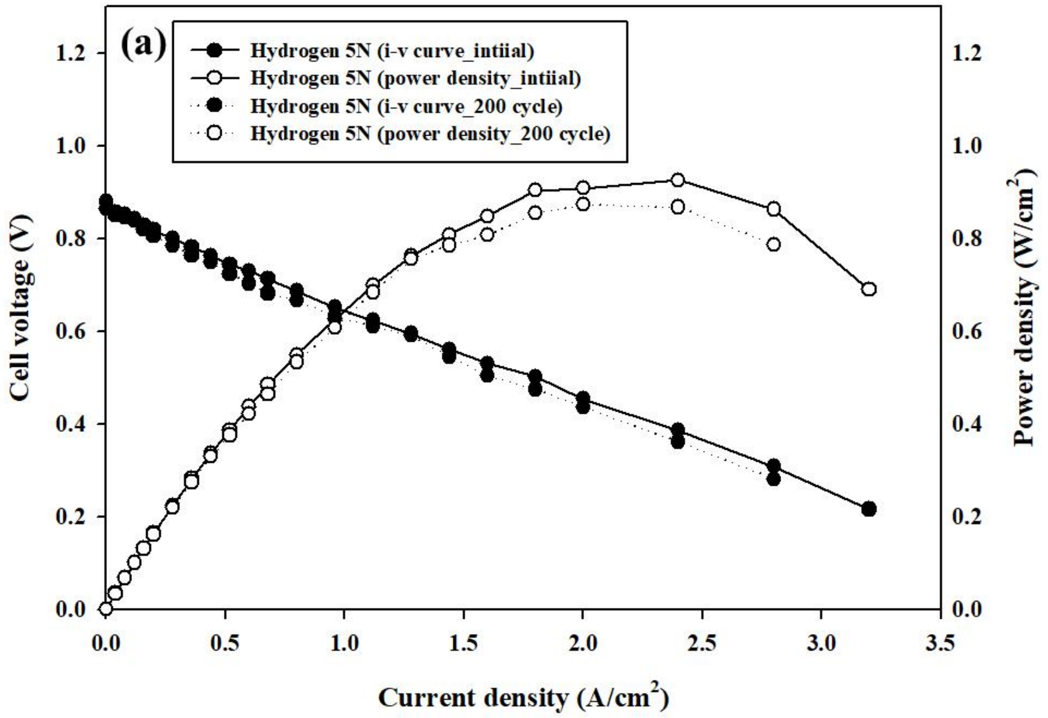
Waste Al type	1 M NaOH solution (120 mins)		3 M NaOH solution		5 M NaOH solution	
	Temperature (℃)	H_2 (mL)	Temperature (℃)	H_2 (mL)	Temperature (℃)	H_2 (mL)
Used beverage cans (A3104)	28	885	38	6,270	43	6,435
De-coated Al can granules (A3104, A5182)	51	5,430	76	6,580	79	6,630
Construction Al materials (A6063)	29	774	37	6,480	40	6,540
Yogurt lids (A8011)	60	4,015	55	4,950	63	5,124
High-purity aluminum (99.99%)	25	362	32	6,710	63	6,855

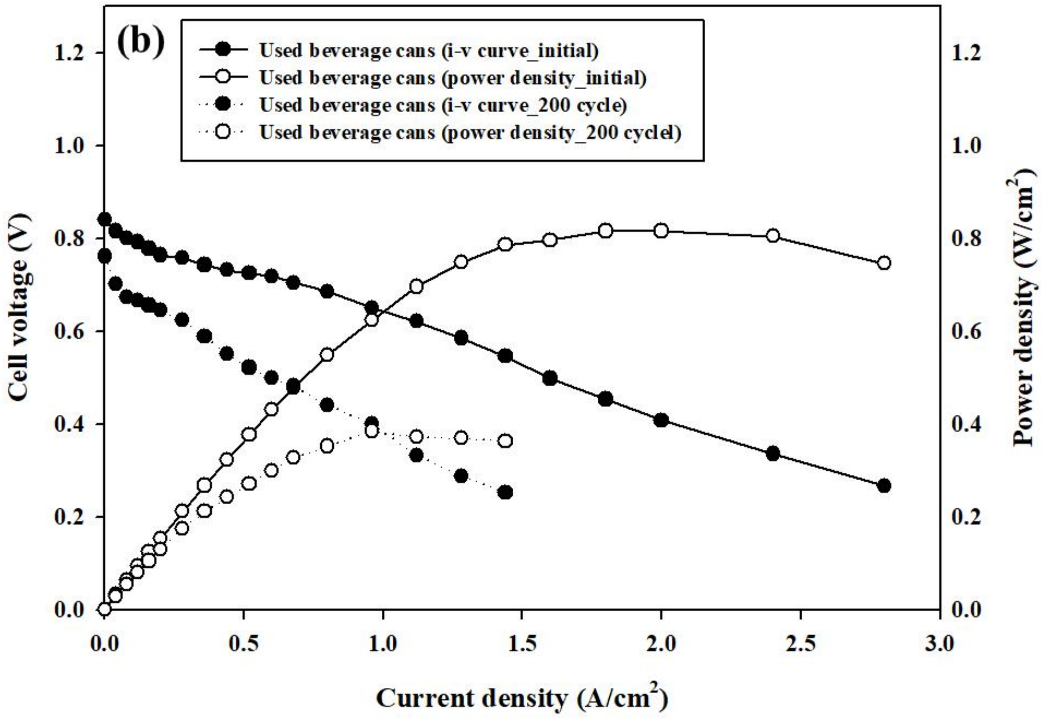
4.2 Fuel cell performance analysis

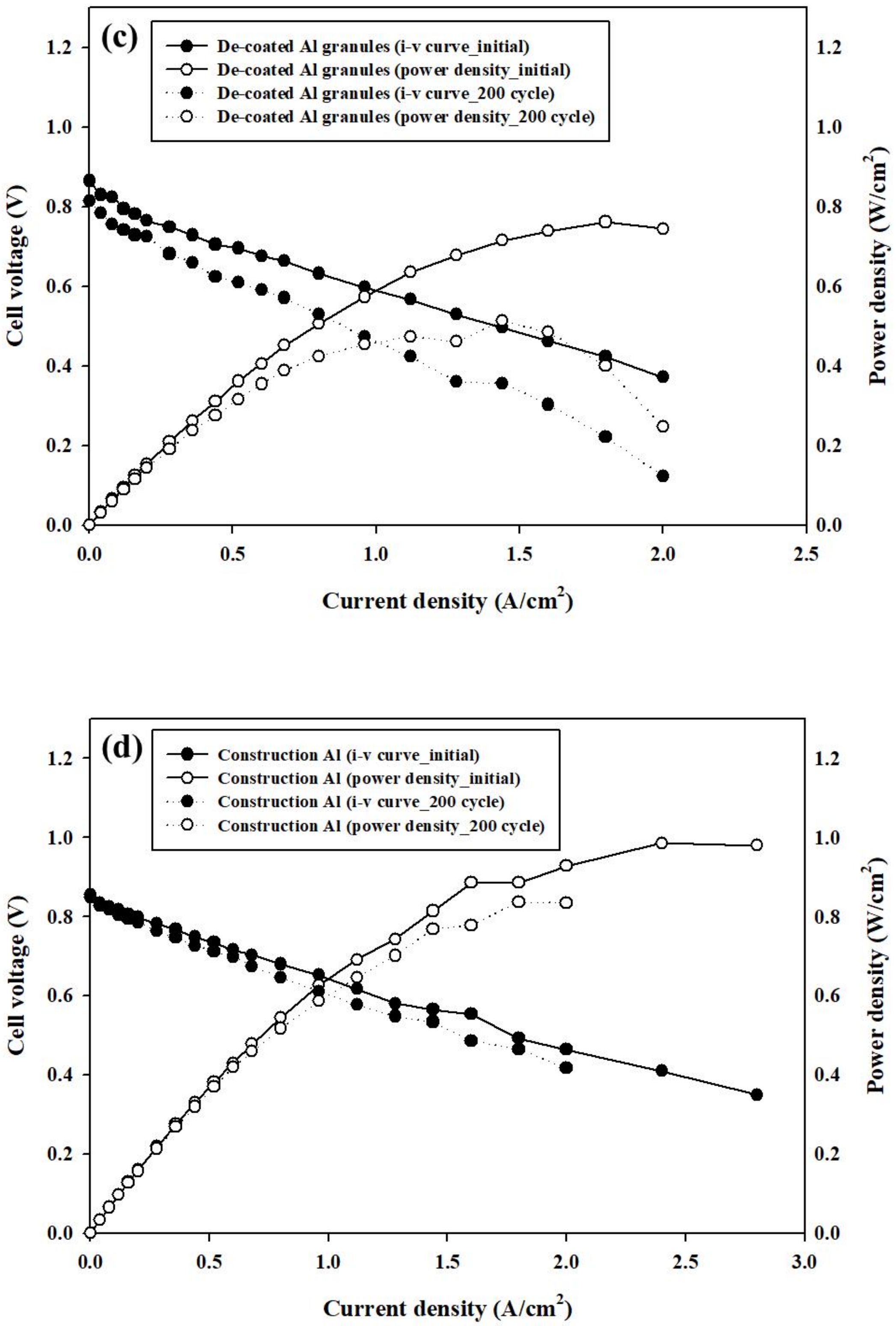
4.2.1 Fuel cell performance

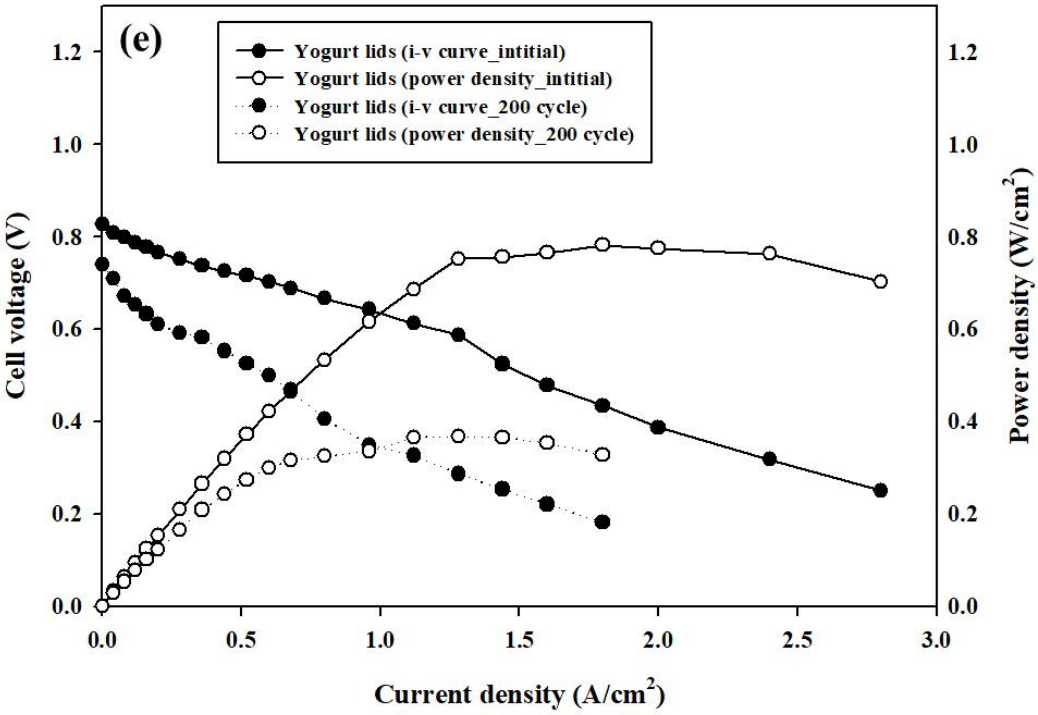
The hydrogen used in this fuel cell performance analysis are high-purity hydrogen (99.999%), UBCs, de-coated Al can granules, waste construction aluminum materials, yogurt lids, and high-purity aluminum (99.99%). When conventional high-purity hydrogen (99.999%) was supplied into the PEMFC, the cell's performance at 0.6 V decreased from 1.25 A/cm^2 to 1.20 A/cm^2 after 200 cycles. In addition, UBCs were reduced from 1.21 A/cm^2 to 0.33 A/cm^2, de-coated Al can granules were reduced from 1.09 A/cm^2 to 0.54 A/cm^2, construction aluminum materials were reduced from 1.20 A/cm^2 to 1.01 A/cm^2, yogurt lids was reduced from 1.20 A/cm^2 to 0.25 A/cm^2, and high-purity aluminum was reduced from 1.27 A/cm^2 to 1.23 A/cm^2.

In the case of high-purity hydrogen (99.999%), commonly used in fuel cells, performance degradation did not occur significantly around 200 cycles. Similarly, it can be seen that performance degradation did not appear significantly in the case of high-purity aluminum. Construction aluminum materials with high hydrogen purity, had some performance degradation compared to high-purity hydrogen and high-purity aluminum, but no significant degradation was confirmed. On the other hand, in the case of UBCs and yogurt lids with a polymer coating on the aluminum surface, performance degradation occurred significantly, and the degree of degradation was similar. In the case of de-coated can granulated after de-coating at UBCs, it can be seen that the coating was removed, resulting in less performance degradation.


(a)
Hydrogen 5N (i-v curve_intiial)
Hydrogen 5N (power density_intiial)
Hydrogen 5N (i-v curve_200 cycle)
Hydrogen 5N (power density_200 cycle)
Cell voltage (V)
Power density (W/cm^2)
Current density (A/cm^2)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5


(b)
Used beverage cans (i-v curve_initial)
Used beverage cans (power density_initial)
Used beverage cans (i-v curve_200 cycle)
Used beverage cans (power density_200 cyclel)
Cell voltage (V)
Power density (W/cm^2)
Current density (A/cm^2)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0


(c)
De-coated Al granules (i-v curve_initial)
De-coated Al granules (power density_initial)
De-coated Al granules (i-v curve_200 cycle)
De-coated Al granules (power density_200 cycle)
Cell voltage (V)
Power density (W/cm²)
Current density (A/cm²)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.0
0.5
1.0
1.5
2.0
2.5
(d)
Construction Al (i-v curve_initial)
Construction Al (power density_initial)
Construction Al (i-v curve_200 cycle)
Construction Al (power density_200 cycle)
Cell voltage (V)
Power density (W/cm²)
Current density (A/cm²)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0


(e)
Yogurt lids (i-v curve_intitial)
Yogurt lids (power density_intitial)
Yogurt lids (i-v curve_200 cycle)
Yogurt lids (power density_200 cycle)
Cell voltage (V)
Power density (W/cm^2)
Current density (A/cm^2)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0

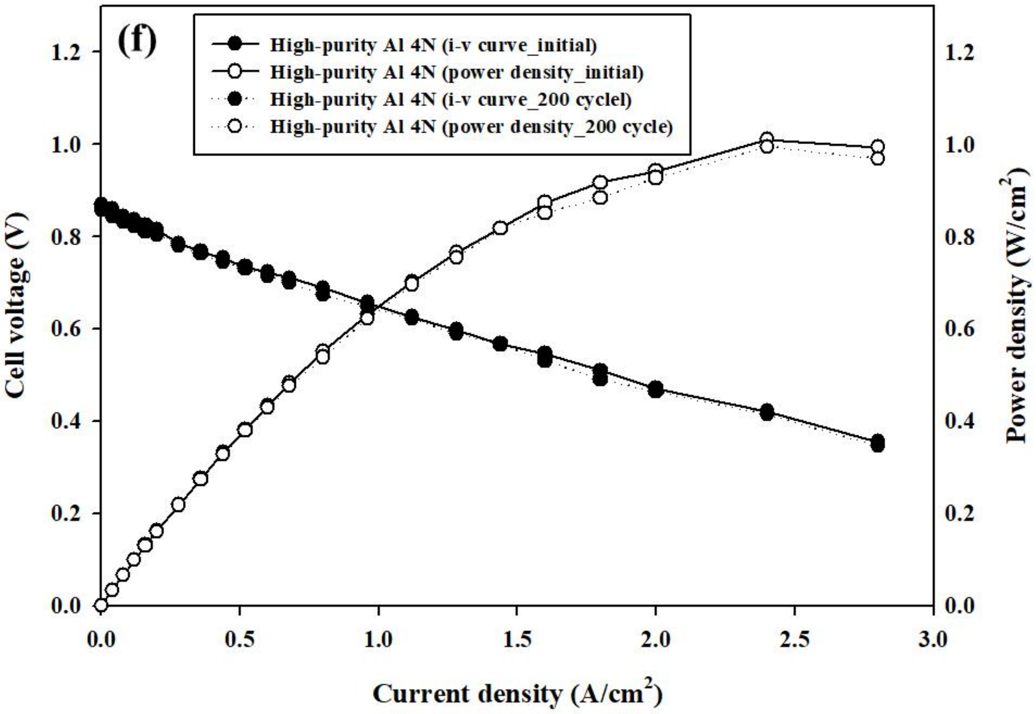


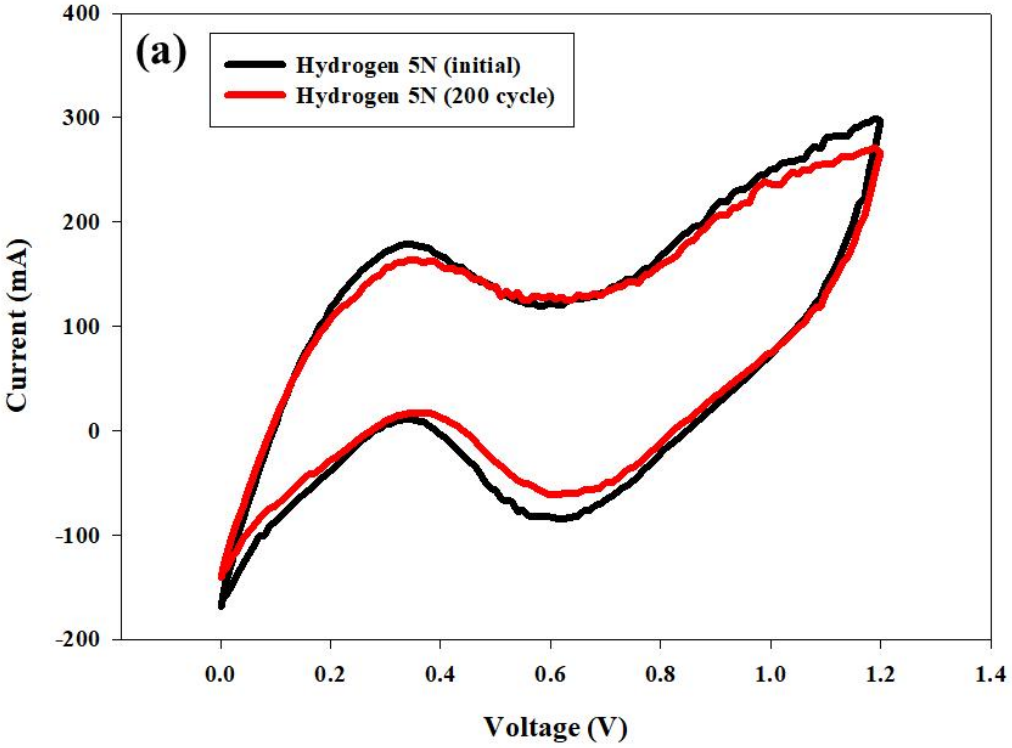
Figure 4-4. Changes in PEMFC polarization curve using waste aluminum composite hydration reaction, (a) Hydrogen 5N, (b) Used beverage cans, (c) De-coated Al can granules, (d) Construction Al materials, (e) Yogurt lids, (f) High-purity Al (99.99%)

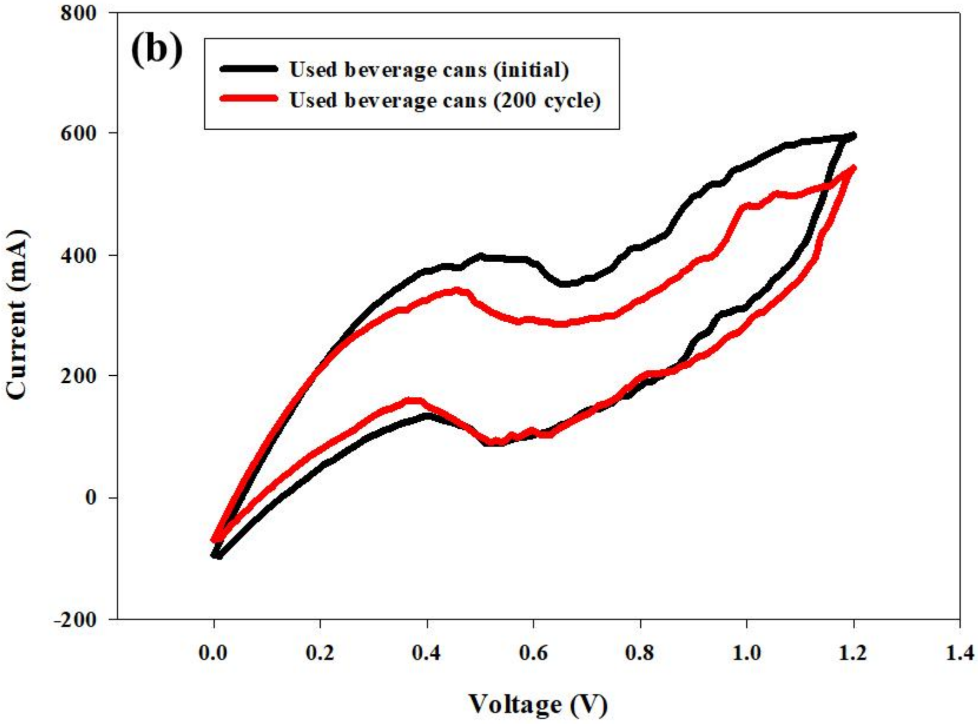
Table 4-5. Changes in power density of PEMFC using different hydrogen

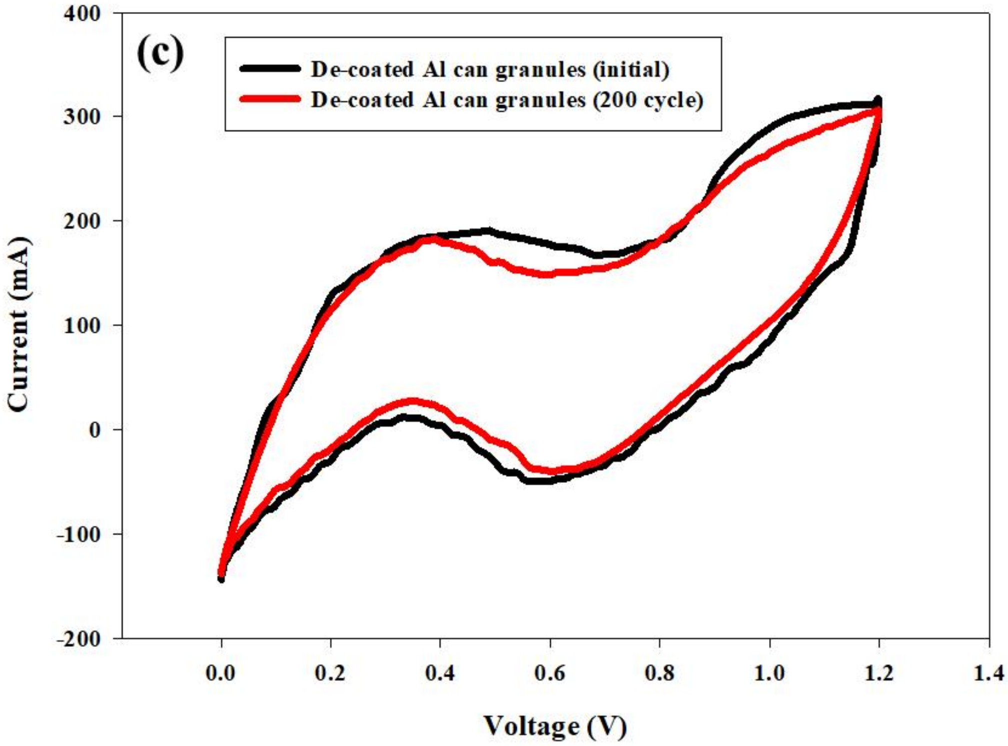
Hydrogen type	Hydrogen (99.999%)		Used beverage cans (A3104)		De-coated Al can granules (A3104, A5182)		Construction aluminum materials (A6063)		Yogurt lids (A8011)		High-purity Al (99.99%)	
Cycle number	0	200	0	200	0	200	0	200	0	200	0	200
current density (A/cm^2 @ 0.6 V)	1.25	1.20	1.21	0.33	1.09	0.54	1.20	1.01	1.20	0.25	1.27	1.23

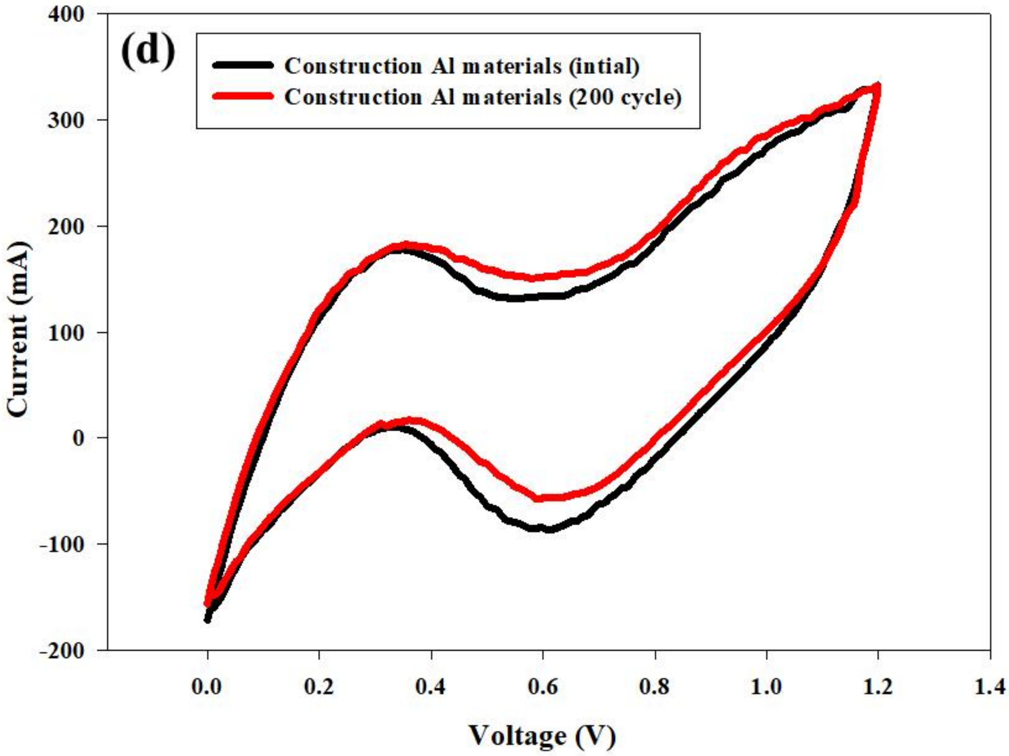
4.2.2 Fuel cell durability

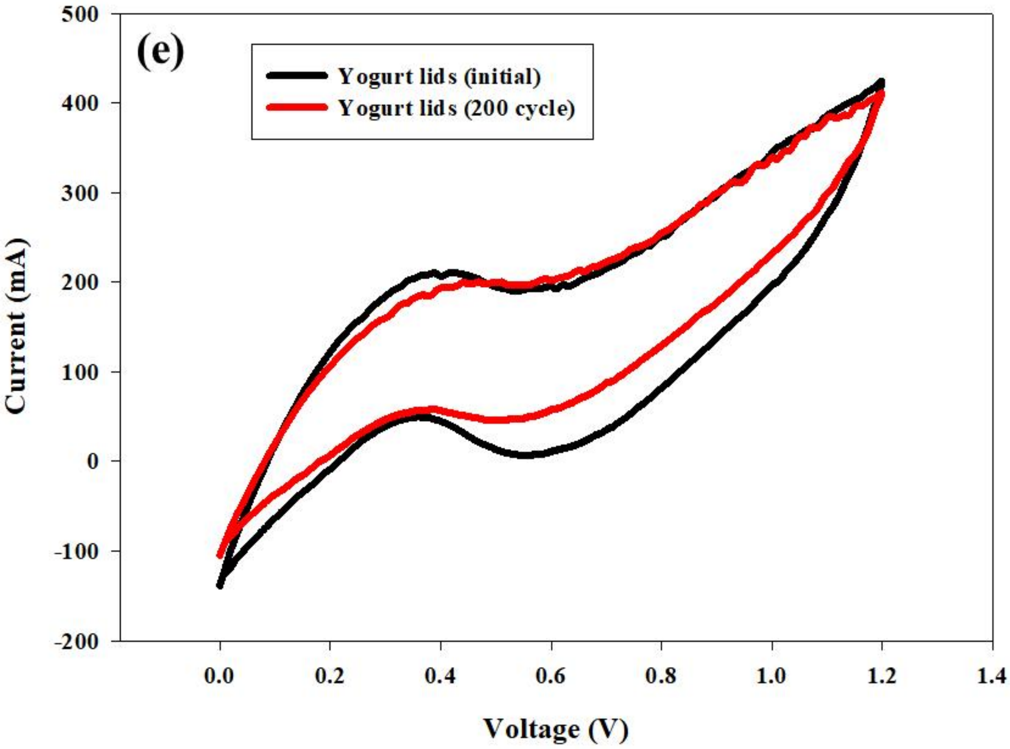
Compared to high-purity hydrogen (99.999%) and other waste aluminum hydration reaction-based hydrogen, significant performance degradation did not occur in cyclic voltammetry (CV) except UBCs and yogurt lids. Unlike other waste aluminum in this experiment, it is considered that the polymer coating on UBCs and yogurt lids directly damage the membrane electrode assembly (MEA) of the fuel cell, and they affect durability. Also, in electrochemical impedance spectroscopy (EIS), the hydrogen-based on UBCs and de-coated Al can granules have high impedance and are greatly affected by charge transfer.




(b)
Used beverage cans (initial)
Used beverage cans (200 cycle)
Current (mA)
Voltage (V)
800
600
400
200
0
-200
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4


(c)
De-coated Al can granules (initial)
De-coated Al can granules (200 cycle)
Current (mA)
Voltage (V)
400
300
200
100
0
-100
-200
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4


(d)
Construction Al materials (intial)
Construction Al materials (200 cycle)
Current (mA)
400
300
200
100
0
-100
-200
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Voltage (V)


(e)
Yogurt lids (initial)
Yogurt lids (200 cycle)
Current (mA)
500
400
300
200
100
0
-100
-200
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Voltage (V)

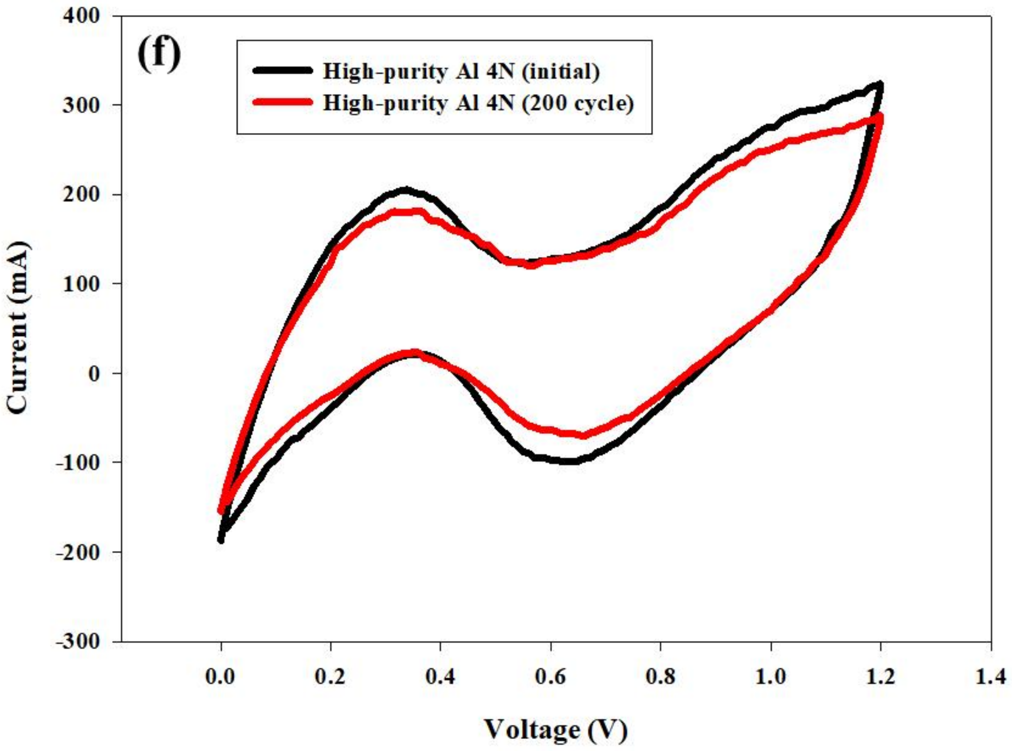
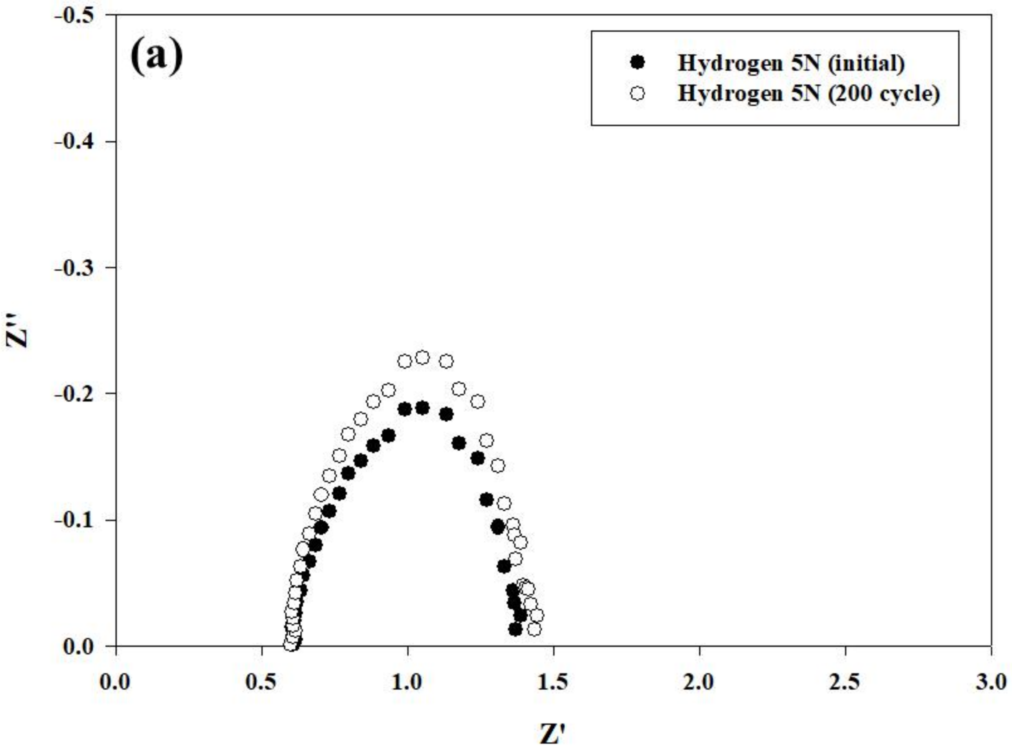
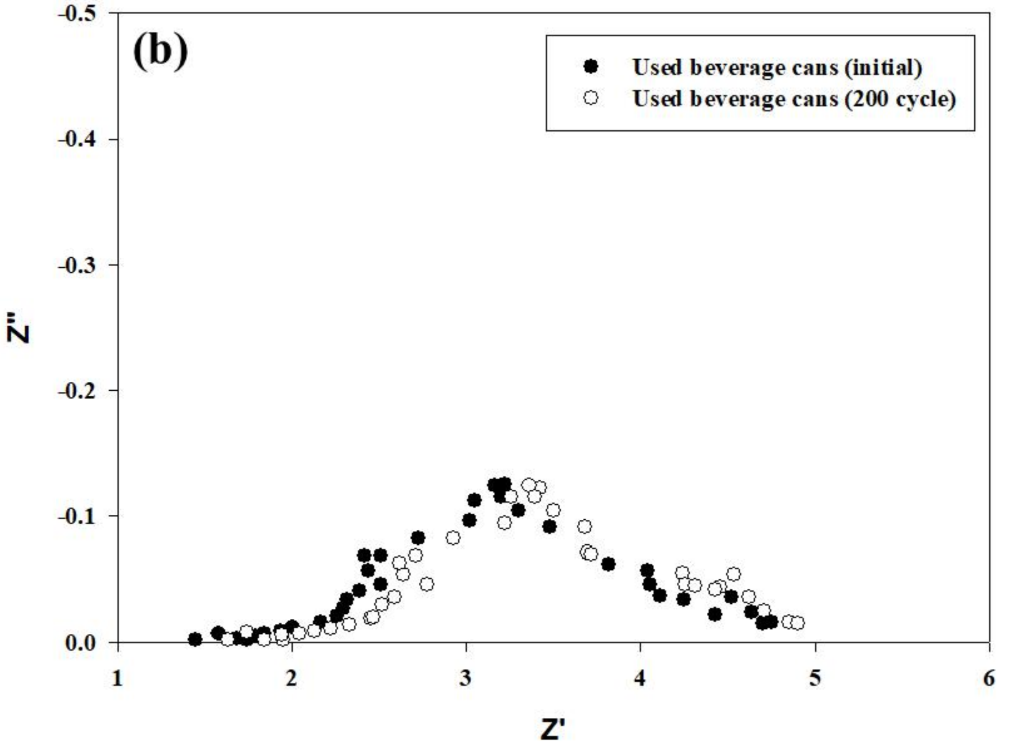
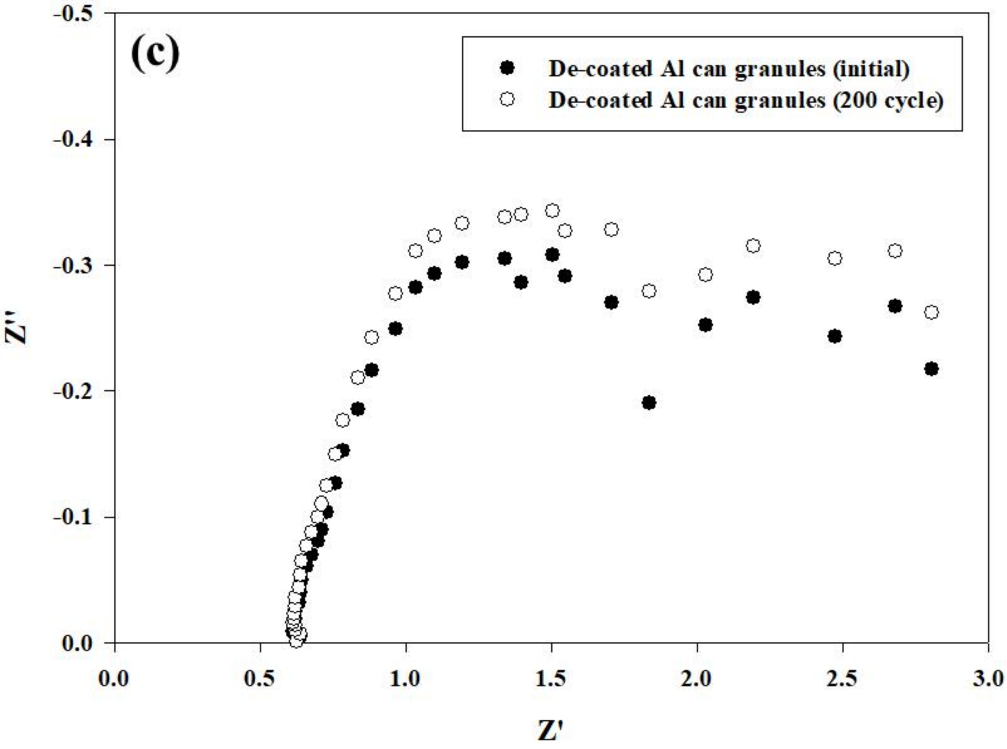
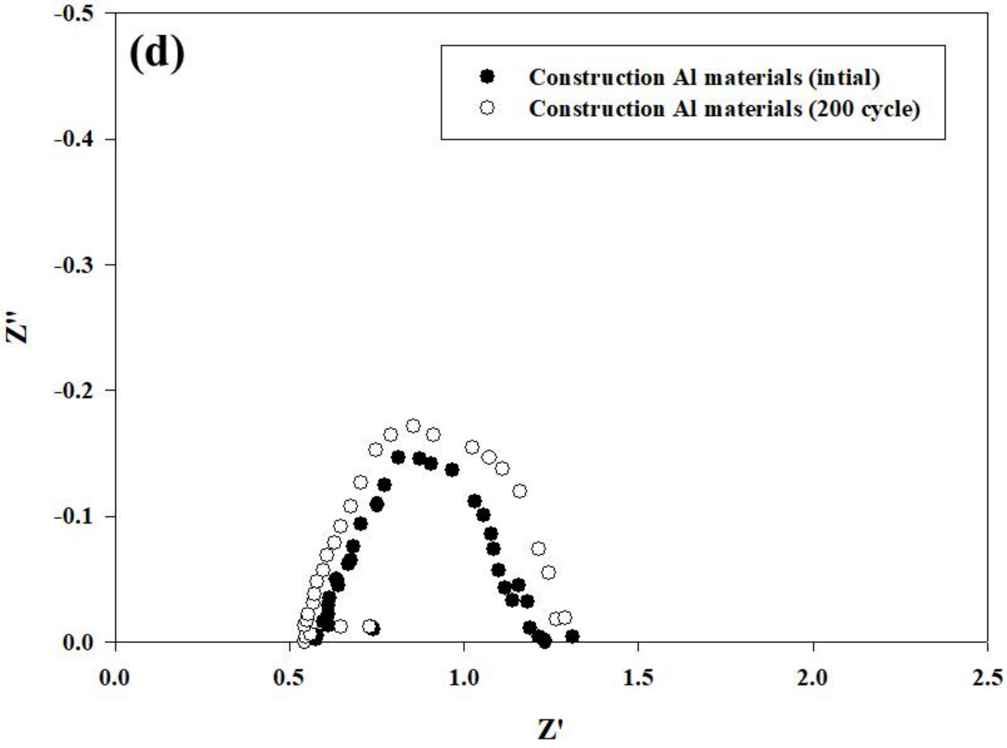


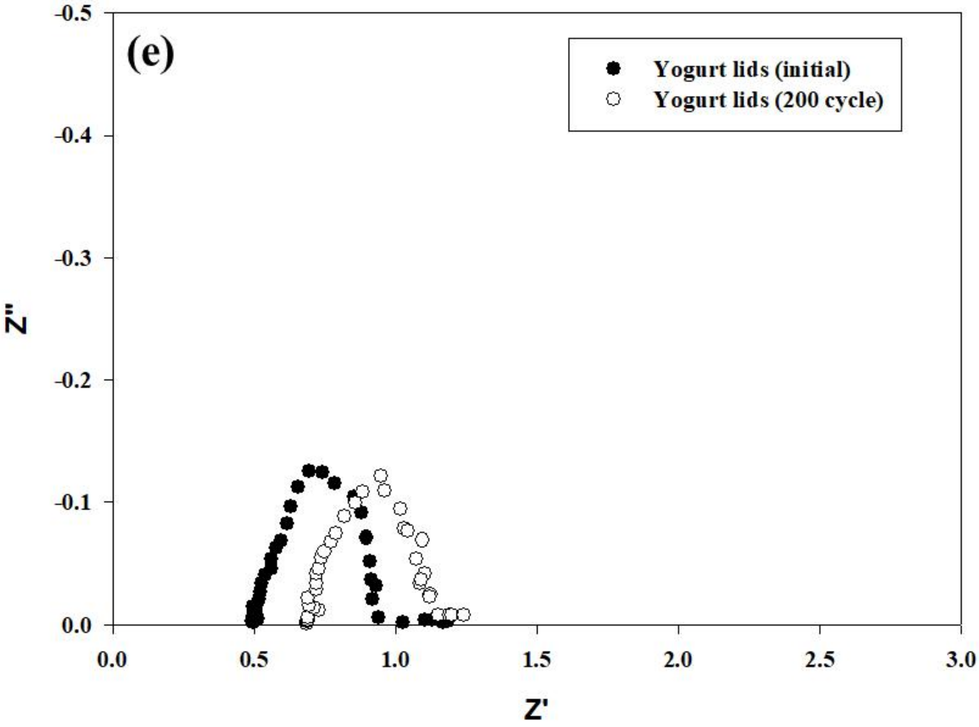
Figure 4-5. Cyclic voltammograms of PEMFC using different kinds of hydrogen, (a) Hydrogen (99.999%), (b) Used beverage cans, (c) De-coated Al can granules, (d) Construction Al materials, (e) Yogurt lids, (f) High-purity Al (99.99%)


(a)
Hydrogen 5N (initial)
Hydrogen 5N (200 cycle)
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
Z''
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Z'


(b)
Used beverage cans (initial)
Used beverage cans (200 cycle)
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
Z''
1
2
3
4
5
6
Z'


(c)
De-coated Al can granules (initial)
De-coated Al can granules (200 cycle)
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
Z''
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Z'


(d)
Construction Al materials (intial)
Construction Al materials (200 cycle)
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
Z''
0.0
0.5
1.0
1.5
2.0
2.5
Z'


(e)
● Yogurt lids (initial)
○ Yogurt lids (200 cycle)
Z''
Z'
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0

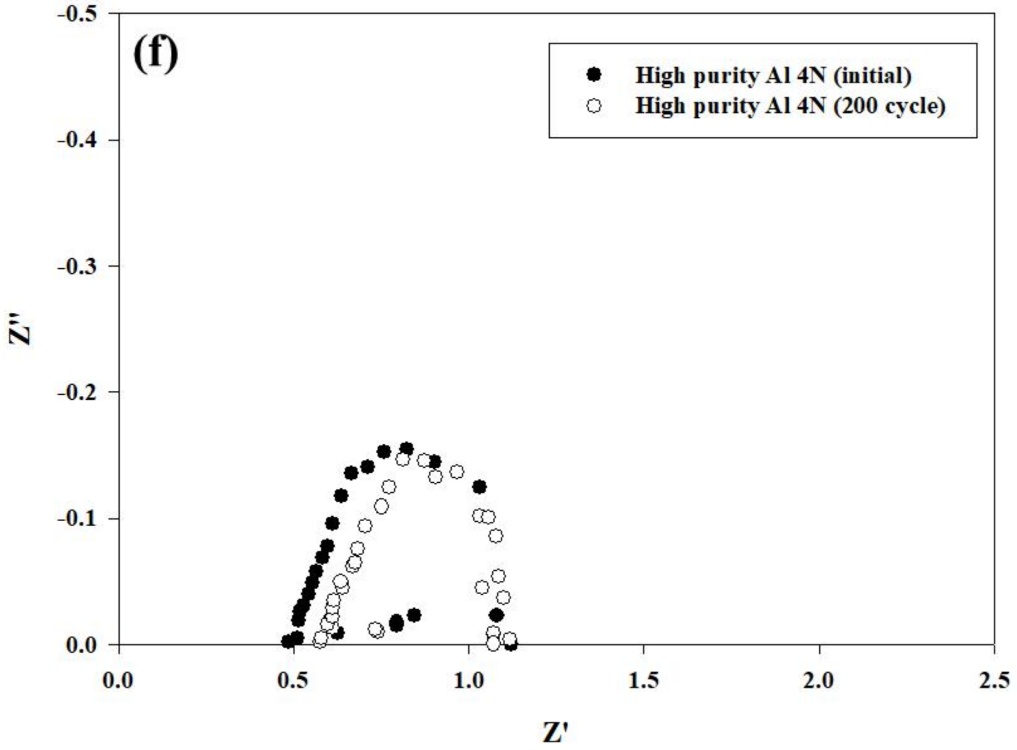


Figure 4-6. Impedance of PEMFC using different kinds of hydrogen, (a) Hydrogen (99.999%), (b) Used beverage cans, (c) De-coated Al can granules, (d) Construction Al materials, (e) Yogurt lids, (f) High-purity Al (99.99%)

5. Conclusions

The waste aluminum hydration reaction was performed with 5 g of waste aluminum and 200 ml of 1, 3, and 5 M of NaOH aqueous solution. The hydrogen production were 6435, 6630, 6540, 5124, and 6855 mL, and the temperature rose to 43, 79, 40, 63, and 63 ℃ respectively when 5 g of UBCs, de-coated Al can granules, construction Al materials, yogurt lids, and high-purity aluminum added with 5 M NaOH solution. In the 3 M NaOH solution, hydrogen was produced in 6270, 6580, 6480, 4950, and 6710 mL, respectively, and the temperature rose to 38, 76, 37, 55, and 32 ℃.

In the application of PEMFC, using conventional high-purity hydrogen (99.999%), the current density of 0.6V was reduced from 1.25 A/cm^2 to 1.20 A/cm^2 after 200 cycles, UBCs was reduced from 1.21 A/cm^2 to 0.33 A/cm^2, de-coated Al can granules were reduced from 1.09 A/cm^2 to 0.54 A/cm^2, construction aluminum materials were reduced from 1.20 A/cm^2 to 1.01 A/cm^2, yogurt lids was reduced from 1.20 A/cm^2 to 0.25 A/cm^2, and high-purity aluminum was reduced from 1.27 A/cm^2 to 1.23 A/cm^2. The impedance measurement showed that UBCs and yogurt lids have high resistance compared to others, while high-purity aluminum and waste aluminum for construction materials showed low resistance.

It is possible to produce a large amount of hydrogen gas easily through the hydration reaction of waste aluminum, and it can also be an alternative to the existing problem of hydrogen gas storage and transportation. However, in the case of PEMFC using a polymer electrolyte membrane, a high concentration of hydrogen gas is required as fuel due to the degradation of the membrane. In the case of hydrogen based on waste aluminum hydration reaction, the concentration of hydrogen gas is somewhat lower than that of hydrogen commercially available as fuel.

Hydrogen generated from construction aluminum materials, had a high concentration of more than 99%, so its initial operating performance was not significantly different from that of high concentration. However, most of waste aluminum hydration reaction-based hydrogen showed more degradation than conventional high-concentration hydrogen when applied to PEMFC operation. Especially, waste aluminum with polymer coating is more degraded, so it is essential to install additional devices to increase the concentration of waste aluminum-based hydrogen gas before supplying to PEMFC.

Reference

Agreement, P. (2015, December). Paris agreement. In Report of the Conference of the Parties to the United Nations Framework Convention on Climate Change (21st Session, 2015: Paris). Retrived December (Vol. 4, p. 2017). HeinOnline.

Balat, M. (2008). Potential importance of hydrogen as a future solution to environmental and transportation problems. International journal of hydrogen energy, 33(15), 4013-4029

Chang, Z., Chen, X., Peng, Y. (2018). The absorption behavior of surfactants on mineral surfaces in the presence of electrolytes - A critical review. Miner. Eng. 121, 66-76.

Choe, B. I. (2020). A Study on the Establishment of Hydrogen Infrastructure Based on Liquid Hydrogen. Superconductivity and Cryogenics, 22(1), 9-12.

Choi, M. H., Choi, J. H., Lee, T. H., Yoo, Y. S. (2011). Effect of Microstructure on Mechanical and Electrical Properties in Ni-YSZ of Anode Supported SOFC. Trans. of the Korean Hydrogen and New Energy Society, 22(5), 592-598.

Chung, K. D. (2019). Economic and Technological Issues of the Hydrogen Economy-Focusing on Value Chain Stage 5. POSRI Issue Report, 2019(5), 1-12.

Dincer, I., Acar, C. (2016). A review on potential use of hydrogen in aviation applications. International Journal of Sustainable Aviation, 2(1), 74-100.

DS-LQUID (n.d.), De-coated Al Can granules, http://www.dsliquid.co.kr/sub.php?code=DP3OK4dd

Ellamla, H. R., Staffell, I., Bujlo, P., Pollet, B. G., Pasupathi, S. (2015). Current status of fuel cell based combined heat and power systems for residential sector. Journal of Power Sources, 293, 312-328.

Guo, Q., Zhou, C., Ma, Z., Yang, X. (2019). Fundamentals of TiO2photocatalysis: concepts, mechanisms, and challenges, Advanced Materials, 31(50), 1901997.

Han, J.-R., Park, J., Kim, Y., Lee, Y. C., Kim, H. S. (2019). Analysis of CO2Emission Depending on Hydrogen Production Methods in Korea. Journal of the Korean Institute of Gas, 23(2), 1−8.

Hiraki, T., Takeuchi, M., Hisa, M., Akiyama, T. (2005). Hydrogen production from waste aluminum at different temperatures, with LCA. Materials transactions, 46(5), 1052-1057.

Hiraki, T., Yamauchi, S., Iida, M., Uesugi, H., Akiyama, T. (2007). Process for recycling waste aluminum with generation of high-pressure hydrogen. Environmental science & technology, 41(12), 4454-4457.

IEA, “The future of hydrogen”, IEA, 2019. Retrieved fromhttps://www.iea.org/reports/the-future-of-hydrogen.

IEA, Global average levelised cost of hydrogen production by energy source and technology, 2019 and 2050, IEA, Paris https://www.iea.org/data-and-statistics/charts/global-average-levelised-cost-of-hydrogen-production-by-energy-source-and-technology-2019-and-2050

IGU. (2020). Global Gas Report 2020.

Im, K. S., Son, T. Y., Jeong H. N., Kwon, D. J., Nam, S. Y. (2021). A Research Trend on Diaphragm Membranes Alkaline Water Electrolysis System, Membrane Journal, The Membrane Society of Korea, 31(2), 133-144.

IRENA (2022), Global hydrogen trade to meet the 1.5°C climate goal: Part III − Green hydrogen cost and potential, International Renewable Energy Agency, Abu Dhabi.

Jayaraman, K., Chauveau, C., Gökalp, I. (2015). Effects of aluminum particle size, galinstan content and reaction temperature on hydrogen generation rate using activated aluminum and water. Energy and Power Engineering, 7(09), 426.

K. Johnson, M.J. Veenstra, D. Gotthold, K. Simmons, K. Alvine, B. Hobein, D. Houston, N. Newhouse, B. Yeggy, A. Vaipan, T. Steinhausler, A. Rau, Advancements and opportunities for on-board 700 bar compressed hydrogen tanks in the progression towards the commercialization of fuel cell vehicles, SAE Int. J. Alt. Power., 6 (2017), 10.4271/2017-01-1183

Kim, J. H., Kim, J. H., Kim, H. S., Ryu, J. H., Kang, S. H., Park, S. M., Jung, S. Y., Lee, S. C. (2020). Recent trends of CO2-free Ammonia Synthesis Technology for Hydrogen Carrier. Journal of Energy and Climate Change, 15(1), 1-22.

Kim, J. H., Lee, E. K., Kim, M. W., Oh, G. W., Lee, J. W., Kim, W. S. (2018). A Study on the Analysis of Safety Standard and Evaluation of Safety Performance for the 5 Nm3/hr Class Alkaline Water Electrolysis System. Journal of the Korean Institute of Gas, 22(6), 65-75.

Kim, J. K., Oh, E. J., Jeong, J. Y., Park, J. N., Kim, Y. S., Lim, H. J. (2019). A Study on the Policy for the Revitalization of Eco-Friendly CO2-free Hydrogen Production. Korea Energy Economics Institute Occasional Research Report, 1-97.

Kim, S. Y., Choi, D. K. (2018). Hydrogen Liquefaction and Storage Technology and Its Application. Korean Industrial Chemistry News, 21(3), 20-28.

Korea Energy Economics Institute (2021). Global hydrogen supply and demand status and future hydrogen supply potential change and response, KEEI Energy Issue Paper, https://www.keei.re.kr/main.nsf/index.html?open&p=%2Fweb_keei%2Fpendingissue.nsf%2F0%2FF16DFD7966B6881B4925849A001DF462&s=%3FOpenDocument%26is_popup%3D1

Lee J. W., Lee, S. I., Kye, D. H., Park, H. J., Park, K. T., Shin, J. Y., Park, W. S. (2021). Numerical investigation of temperature distribution on solid oxide electrolysis cell. The Spring and Autumn Conference of the Korean Society of Mechinical Engineers, 1314-1317.

Lee, J. H. (2022). A Research Trend on the Anion Exchange Membrane for Water Electrolysis. NICE (News & Information for Chemical Engineers), 40(5), 498-506.

Lee, J. Y., Yi, Y. M., Uhm, S. H. (2008). Understanding Underlying Processes of Water Electrolysis. J. Korean Ind. Eng. Chem., 19(4), 357-365.

Park, J. H., Kim, C. H., Cho, H. S., Kim, S. K., Cho. W. C. (2020). Techno-Economic Analysis of Green Hydrogen Production System Based on Renewable Energy Sources. Trans. of Korean Hydrogen and New Energy Society, 31(4), 337-344.

Rosenband, V., Gany, A. (2010). Application of activated aluminum powder for generation of hydrogen from water. International Journal of Hydrogen Energy, 35(20), 10898-10904.

Sekine, Y., Higo, T. (2021). Recent trends on the dehydrogenation catalysis of liquid organic hydrogen carrier (LOHC): A review. Topics in Catalysis, 64(7), 470-480.

Shmelev, V., Nikolaev, V., Lee, J. H., Yim, C. (2016). Hydrogen production by reaction of aluminum with water. international journal of hydrogen energy, 41(38), 16664-16673.

Sim, W. J., Na, I. C., Song, M. H. Chung, H. B., Kim, J. H., Kim, T. H., Park K. P. (2009). Hydrogen Production by the Reaction of Al and Alkaline Solution for PEMFC Application. Trans. of the Korean Hydrogen and New Energy Society, 20(1), 1-8.

Staffell, I., Scamman, D., Abad, A. V., Balcombe, P., Dodds, P. E., Ekins, P., Shah, N., Ward, K. R. (2019). The role of hydrogen and fuel cells in the global energy system. Energy & Environmental Science, 12(2), 463-491.

Tugsataydin (2017), File:Galvanic series noble metals.jpg, Wikimedia commons, https://commons.wikimedia.org/wiki/File:Galvanic_series_noble_metals.jpg

United States Department of Energy (2021), Hydrogen shot summit, https://www.energy.gov/eere/fuelcells/hydrogen-shot-summit

United States Department of Energy (n.d.), Hydrogen storage, https://www.energy.gov/eere/fuelcells/hydrogen-storage

Xu, S., Cui, Y., Yang, L., Liu, J. (2020). Instant hydrogen production using Ga-In-Sn-Bi alloy-activated Al-water reaction for hydrogen fuel