A Review of Spent Lead-Acid Battery Recycling Technology in Indonesia: Comparison and Recommendation of Environment-friendly Process

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Abstract. Indonesia is one of the largest recycler of Lead Acid Battery (LAB) in Asia suffering for lead contamination which is classified as one of the top poisonous heavy metal pollutant. The corresponding Issues have already caused significant public concern. This paper describes a brief overview and comparative study of some pyro metallurgy and hydrometallurgy processes by collecting data of input materials, energy consumption, environmental impact and main products. Subsequently, mass flow of lead and entire cycle of lead recovery process is calculated semi-quantitatively. According to the result, some of primary lead recycling processes can be cut off along with minimizing environmental issues due to the emission products, if the proper management of waste is implemented. This research provides a guideline for the saver life cycle of recovering lead from spent lead paste of LAB aiming to contribute for green efficient cycle of secondary lead in Indonesian Industry.

1. Introduction

Lead (Pb) as the major component of spent lead acid battery is a hazardous material causing extensive environmental contamination and human health. Smelter not only emits ash as the waste product yet also Pb particle through the air and contaminates the land in such radius of the recycling plant. Haryanto, 2016 found that many children in the areas nearby the Pb smelter were having difficulty achieving high grades at school and having problem with physical development [1]. Furthermore, the same research also showed that some of chronic health problem caused by blood lead level increased by almost doubled compared from the data in 2011 and 2015. Pb is highly toxic poisoning organs through blood flow. Adults exposed to lead salt for a long time severe to nephropathy and decrease performance of nervous system [2,3].

Although it shares some drawbacks, secondary lead plant in Indonesia remain stood as economic commodity due to its value which significantly lowering production cost of primary lead.

Compare to other battery, lead acid battery dominated market shared of power back-up system since it has high operational safety, portable application and established recycling technology. The growth of vehicle in Indonesia contributes to the increasing of lead acid battery numbers as well as its waste. As all of the components of this electrochemical battery are recyclable, there are some recycle plants of spent lead acid growth in developing country including Indonesia. The distribution of spent lead acid battery plants in Indonesia is spread all over the country with more than 200 battery recycling smelter (Figure 1).

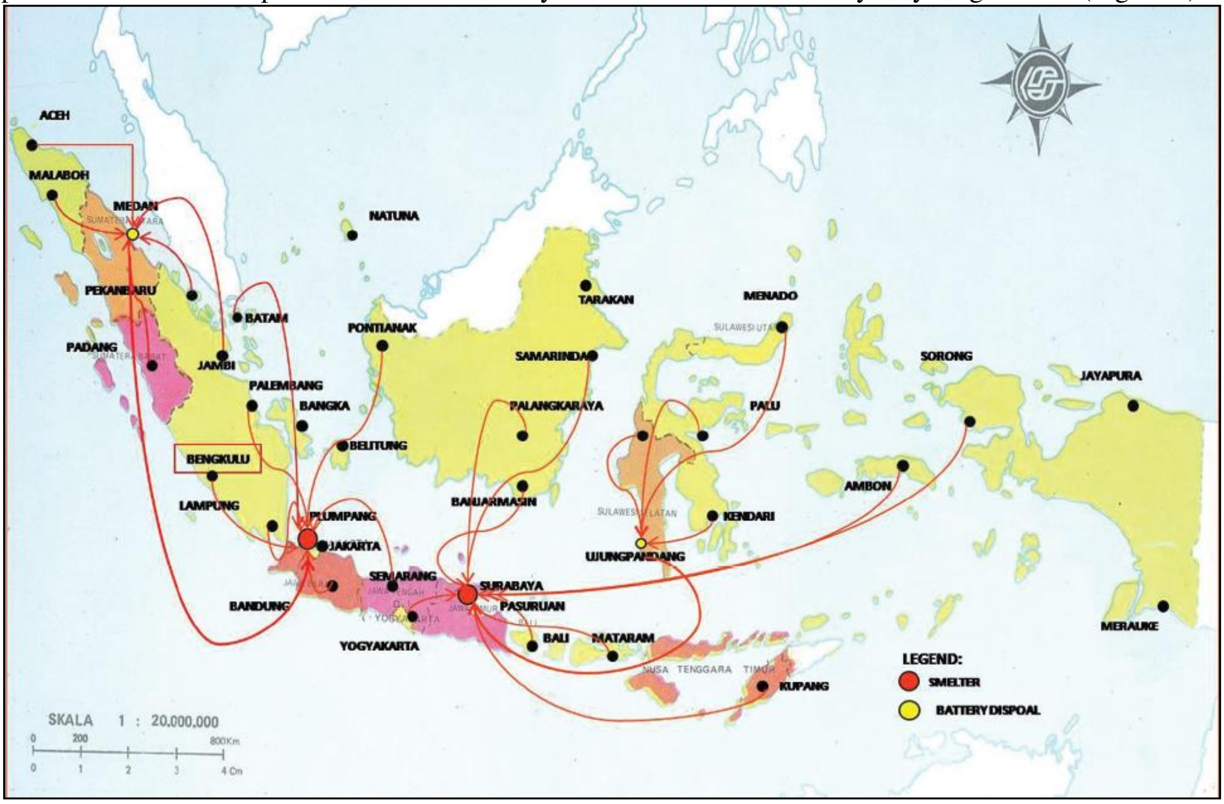

Figure 1. Distribution of lead acid battery smelter in Indonesia, [1]

Recycling of lead acid battery has become serious problem to environment, if it not handled properly. The technology of recovering lead from spent lead acid battery may contain various scheme either it pyrometallurgy or hydrometallurgy. Most plants in Indonesia treat these electronic waste pyrometallurgycally by smelting process. Processing every component by melts the raw material toward its liquid state. Yunjian Ma and Keqiang Qiu [4] predicted that lead based material will increase in the next several years due to leveling up of automotive vehicle numbers, yet primary lead production remains static. There for recycling lead as secondary source is essential for this industry development.

As nowadays the increasing concern of the environmental problems require special regulation, spent lead battery process needs more attention both from industry and research institution. In this paper the overview and comparison of recycling technology of lead acid battery is being discussed to identify the most appropriate technology to recovery these hazardous material.

Since vehicle growth is one of the key factors affecting spent lead acid battery recycling resource, here it is Figure 2 illustrating the number of motorcycle in Indonesia during 2001 to 2015 [5].

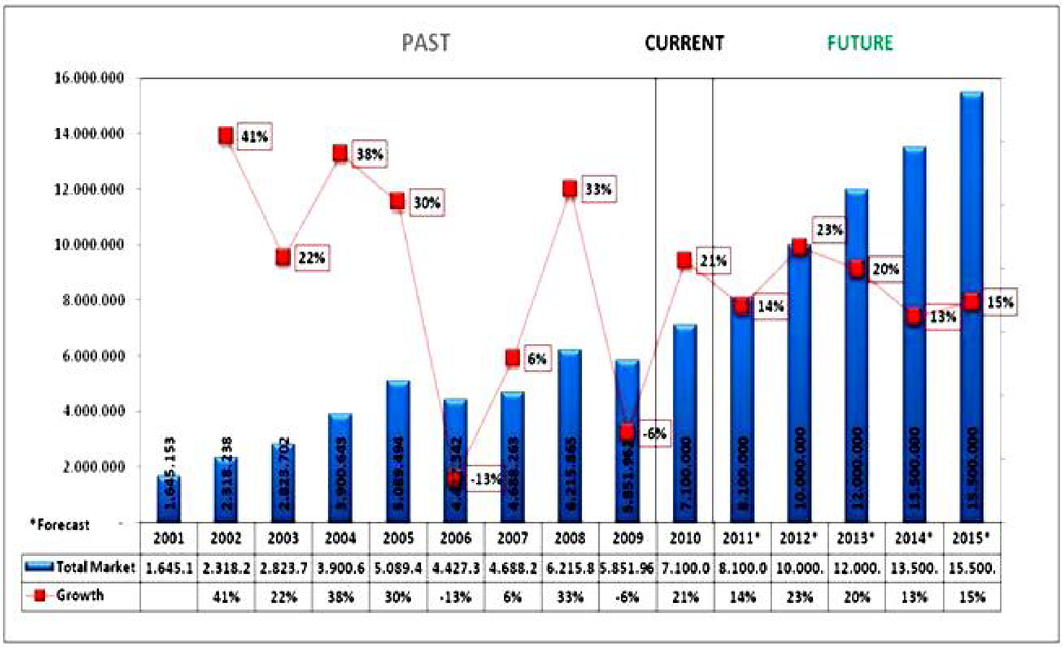

Figure 2. Suzuki Report of National Motorcycle Market and Prediction

The graph above shows that motorcycle numbers in Indonesia improved toward positive trend and it will impact the need of battery particularly lead acid battery. With the average working life under normal conditions, is 3 to 4 years. Technavio predicted that the lead acid national battery market will grow at a CAGR of 3.6% over the period 2014-2019 [6]. Zang, 2016, depict the comparison of lead consumption either from primary source or secondary on the following graph [7].

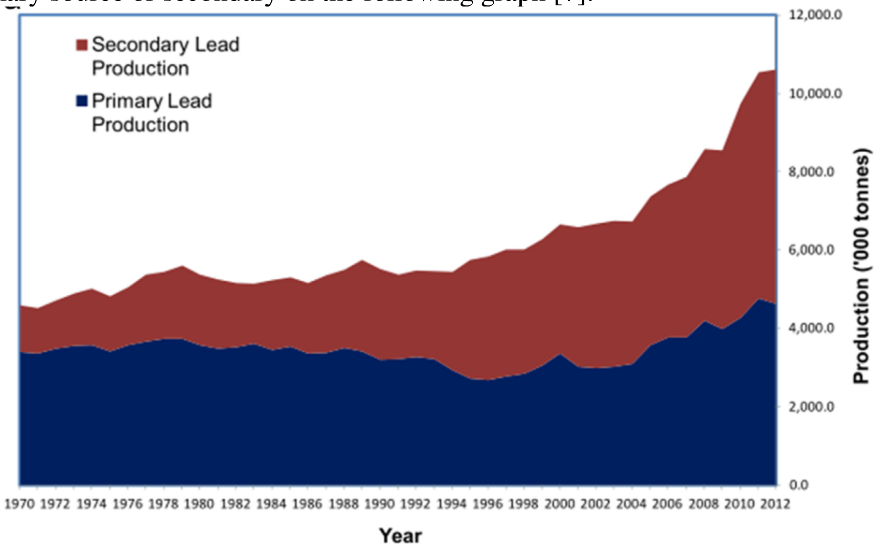

Figure 3. The amount of secondary and primary lead production from 1970 to 2012

2. Processing scheme

Recycling technology of spent lead acid battery are available either metallurgical or chemical with some pretreatment process such as breaking, crushing and physical separation. In general, spent battery separated into lead 24-30 wt% grit electrode, 11-30 wt% electrochemical solution [8], 30-40 wt% lead

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paste, polypropylene separator and plastic box materials [9,10,11]. The composition of recycling raw materials is shown in Table 1 (taken from composition data of W accu NS70 and other research data). It can be found that spent lead acid battery dominates by grit or electrode plate followed by electrolyte, connector, box and separator.

Table 1. Composition ratio of spent lead acid battery [10,11,12] 13,7

Sample	**Constitutions, wt.%**					
	Grid	**Lead Paste**	**Shell**	**Electrolyte**	**Separator and Others**	
W NS70	35,0	35,8	8,7	20,4	14,6	
1	30,7	34,7	5,9	25,1	3,6	
2	28,2	35,7	5,0	28,6	2,5	
3	26,2	34,6	17,7	18,7	2,8	
4	24,7	31,2	16,9	25,0	2,2	
5	25,0	38,0	10,0	22,0	5,0	
6	28,7	40,3	5,5	21,3	4,2	

		Composition, wt%					
		Pb	**PbO**	**PbO_2**	**$PbSO_4$**	**Sb**	**Density, g/cm^3**
Spent battery	**Grid**	92-95	Minor	Minor	Minor	3-6	9,4
	Paste	N/A	10-15	15-20	25-30	~0,5	3,3
New Battery	**Grid**	92-95	Minor	Minor	Minor	3-6	9,4
	Paste	N/A	~100	Minor	Minor	N/A	N/A

2.1. High temperature process (pyrometallurgy)

Most lead recyclers all over the world process the raw materials throughout smelting process as this process is easy to operate with relatively unskilled workers. Lead-acid batteries are recycled pyrometallurgically with initial physical separation, followed by sulfur removal, smelting and refining process. Figure 2 provides flow diagram of general recycling process of lead acid battery. Many smelters have installed leaching plant to remove sulfur prior to smelting process, this step significantly lowers temperature operation during smelting process and subsequently minimize production cost. The other benefit contributes by this process are, processing $PbSO_4$ toward alkali sulfate will reduce SO_2 emission, minimize slag production and decrease the generate matte [13].

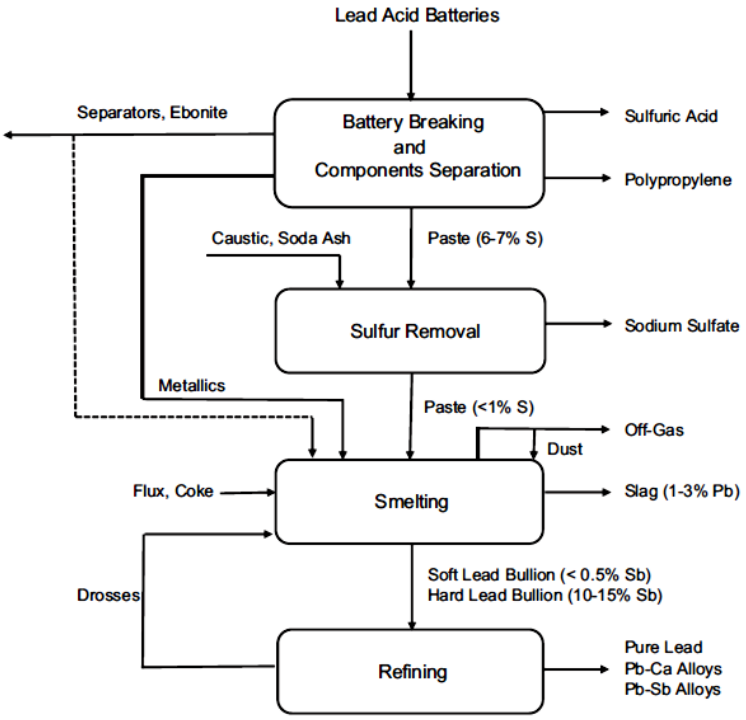

Figure 4. General recycling process of lead acid battery [13]

Lead acid usually have stable composition, it can be immediately fed to the furnace and processed in relatively low temperature (depend on Pb's melting temperature). Meanwhile it does not work for lead paste which requires more complex process to remove sulfur. Some reaction conducts in smelting process involving flux and reductant materials is as follows [14]. It is called direct process.

$PbSO_4 + Na_2CO_3 \rightarrow PbO + Na_2SO_4 + CO_2$………………………………………….. (1)

$PbO_2 + Fe \rightarrow PbO + FeO$……………………………………………………….. (2)

$2PbO_2 + 2Fe + C \rightarrow 2Pb + 2FeO + CO_2$.. (3)

While the reaction of indirect process which initially began by desulfurized paste using caustic or soda ash as a leaching agent is as bellow [12]:

$PbSO_{4\,(paste)} + 2\ NaOH_{(aq)} \rightarrow PbO_{(paste)} + Na_2SO_{4(aq)} + H_2O$……………………………. (4)

$PbSO_{4\,(paste)} + Na_2CO_{3\,(aq)} \rightarrow PbCO_{3\,(paste)} + Na_2SO_{4(aq)}$………………………………….. (5)

This leaching agent used to fix S as soluble $Na_2SO_{4\,(aq)}$ which can be crystallized out as a saleable by product. The insoluble $PbCO_3$ or $Pb(OH)_2$ collected as sludge or filter cake. Unfortunately, S contamination in filter cake which always associated with SO_2 emission, could not be fully avoided [15].

The reverberator furnace, blast furnace, electric arc furnace or combinations is seen commonly used to recycling lead via pyrometallurgical process. In which the charging materials consist of not only grid and paste but also flux, coke and reductant materials. Conventionally in Indonesia some illegal smelters process this battery spent using an open furnace (Figure. 3) which not only danger some people in charge but also people around the smelter area. Pb particle could directly attack respiration system and distributes toward blood toward neuro-system. Indirectly Pb particles contaminate the ground and water affecting the local harvest product which further consumed. Dusts and slags from lead processing can dissolve in aqueous system which harmful to the environment.

Figure 5. Open furnace process, conventionally used by some smelters in Indonesia

Despite the fact that high temperature technology has made such improvement toward energy efficiencies yet the environmental problem concerning this issue boomed more significantly. A study shows that family who had engaged in recycling of spent batteries indicating neurological disorders (legs and hands muscles weakness), blood lead levels were more than 30 µg/dL and mental retardation in two people [1].

Figure 6. Traditional oxygen bottom blowing process

Another pyrometallurgicall method commonly done in Indonesia is oxygen bottom blowing furnace Fig. 4. Compare to the previous process this kind of smelting treatment combining energy efficiencies and environmental-friendly factors. Though the issues of lead containing slag and SO_2 gas is still need special concern [2,15].

Based on processing furnace which employed, the smelting treatment technology can be designed as the QSL process, Isasmelt Paste Smelting process, Kivcet method, Kaldo smelting process, Rotary and Reverberatory furnace.

Despite the fact that the high temperature process has contribute to economic and energy efficiencies, its byproduct namely dust containing lead particulate easily contaminates the environment and poisons human, animal, bird, soil and drinking water. The study shows that in China, children near the spent lead smelter severe from 50,1 µg/kg/d blood containing lead which is Haryanto, 2016, in his research said that this percentage will damage the blood forming system. The amount of lead particulate emissions and also SO_2 must be reduce trough the qualified production standard followed by updating technology of secondary lead production and its infrastructure [1].

2.2. Low temperature process (hydrometallurgy)

Considering environmental issue hydrometallurgy combined by electrowinning process offering alternative route which clime to be eco-friendly process. Hydrometallurgy not only used for removing sulfur from the charge materials but also offered a primary stage itself. Although this process is time depending, these kinds of processes have high energy efficiencies as it conducted in room temperature. Hydrometallurgical process converses lead sulfate to lead carbonate, hydroxide or hydroxocarbonate toward following reaction [13].

$$PbSO_{4(S)} + 2NaOH_{(aq)} \rightarrow Pb(OH)_{2(aq)} + Na_2SO_{4(aq)} \quad (6)$$
$$PbSO_{4(S)} + Na_2CO_{3(aq)} \rightarrow PbCO_{3(s)} + Na_2SO_{4(S)} \quad (7)$$
$$3PbSO_{4(S)} + 4Na_2CO_{3(aq)} + 2H_2O \rightarrow Pb_3(CO_3)_2(OH)_{2(S)} + 3Na_2SO_{4(aq)} + 2NaHCO_3 \quad (8)$$
$$2PbSO_{4(S)} + 3Na_2CO_{3(aq)} + H_2O \rightarrow NaPb_2(CO_3)_2OH_{(s)} + 2Na_2SO_4 + NaHCO_{3(aq)} \quad (9)$$

Hydrometallurgical process involves leaching method where lead selectively solves in relatively low temperature. Lead paste can be converted to soluble sulphate by reacting with chemical reagents. This subsequently reduces the air emission, since there is almost no gas stage product. Besides, lowering temperature will significantly cut down energy consumption.

In this type of process, the desulphurization process is strongly affected by diffusion and mass transfer limitation of $PbSO_4$ and Na_2CO_3 due to high density of lead paste in traditional reactor [16]. Concerning of this condition, the high grade soluble lead only yield after relatively long reacting time. So it is significant to manufacture a high mass transfer efficiency reactor for such a high density liquid-solid system. The following picture show the core-shell structure of the desulphurization of lead sulfate leaching in the citric acid solution.

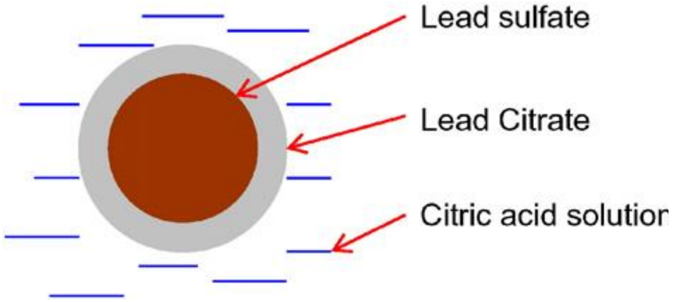

Figure 7. Core-shell structure of the desulphurization of lead sulphate

Kumar et al. invented the patented technology of recycling lead-acid batteries using a citric acid and sodium citrate solution. In this method, lead is recovered in the form of ultra-fine lead oxide powder after calcining the lead citrate precursor, and the lead oxide can be directly used for making new batteries, thus circumventing the oxidation step from metallic lead [17,18,19].

Although the SO_2 release problem is solved in the hydrometallurgical process, hazardous gases containing fluorine appear in the electrowinning process. Meanwhile, the electro-winning process is capitally intensive and usually only suitable for large-scale operations. The process using citric acid and sodium citrate provide a convenient and environment-friendly approach for recycling lead paste. However, citric acid is much more expensive than sodium carbonate [20].

Compare with the pyrometallurgical method, hydrometallurgy followed by electrowinning process was less economically favorable with higher production cost [20]. As calculated, the energy cost per matric ton PbO output of electrowinning route was 50 US$ higher than its of pyrometallurgal method. Furthermore, toxic reagents are often engaged in this process which not only dangerous to human health yet also to metallic component of the equipment severe from corrosion.

Other hydrometallurgical method which could be used to produce secondary lead are in which this leaching procedure followed by either cementation or calcinations. In general, this process eliminated the emission of SO_x, NO_x, and lead particulate and reduced energy consumption. However, cementation process requires additional reduction agent such as iron to increase recovery ratio which impact to the accumulation of iron impurity.

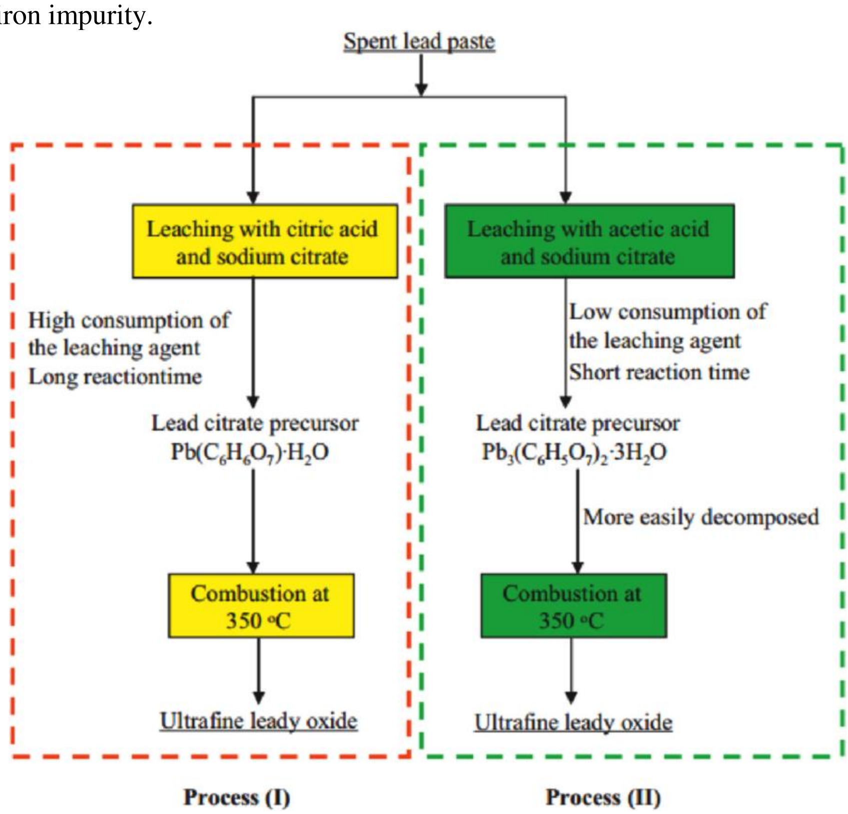

Figure 8. Flow diagram of two leaching procedures followed by low temperature calcination

A new green hydrometallurgical process demonstrated by Pan at al, which considerably reduce lead exposure to the environment [21, 22, 23]. This method recovers lead by establishing fuel cell unit in which H_2 was fed into the anode as the following figure.

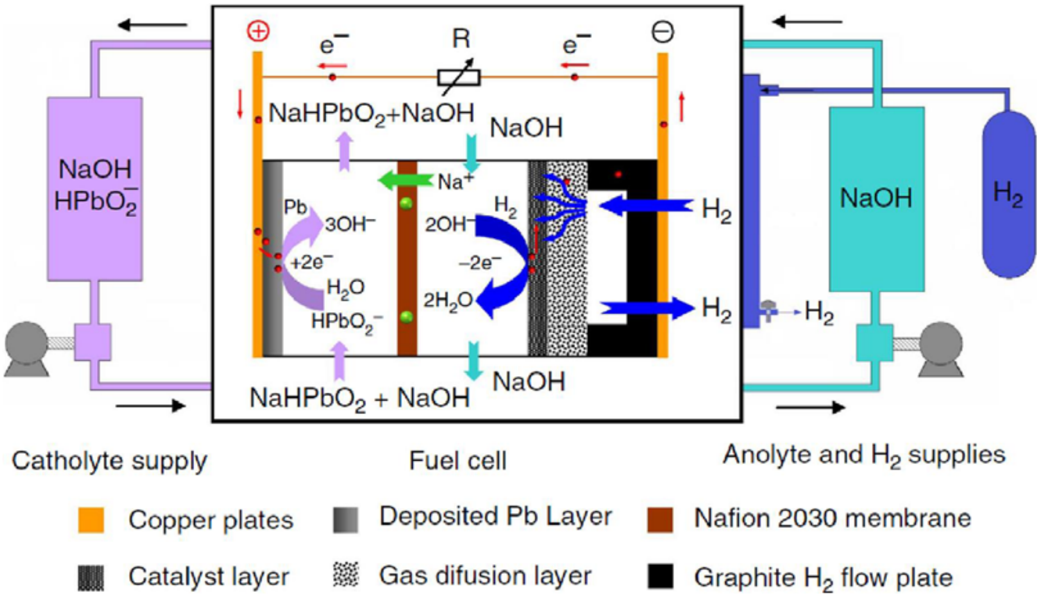

Figure 9. The schematic of the H_2-PbO fuel cell

This novel procedure eliminates the environment issue associated with pyrometallurgical process. As byproduct electricity can be produced throughout this process by only reducing water. However, there still have to be considered for long term running plant since this process is time dependent.

3. Conclusion

Since secondary lead recycling from spent lead acid battery is prospective for lead metal alternative resource and positively affect economic growth, the term of environmental issue due to this processing activity must be strictly concerned. Despite lead smelting route which commonly used give significant impact to secondary lead yield, the environment issue toward emission was a major drawback. So, the electro hydrometallurgical process which clime as the eco-friendly procedure was developed yet the longer period, high investment for resulting secondary lead still taking concern. Innovative environment friendly method must be proposed and developed. The spent paste to the new paste method seems to be the most recommended process to produce new battery and minimize gas pollution.

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