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Recovery of nano-Al_2O_3 from waste aluminum electrolytic solution generated during the manufacturing of capacitors

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ABSTRACT

The purpose of this study was to develop a resource recovery procedure for recovering nano-Al_2O_3 from the waste aluminum electrolytic solution generated during the manufacturing of capacitors. The high concentrations aluminum contained in electrolytic solutions have a high resource potential and economic value. In this study, the co-precipitation method was used to recover the waste aluminum electrolytic solution. The results show that the purity and particle size of the recovered Al_2O_3 were 99.943% and 0.174 μm, similar with the commercial Al_2O_3 powder. Additionally, about 80% of the used ammonia could be recycled and reused in the reaction process. The processing technology presented in this work is thus feasible, and the application methods and economies of scale achievable with this approach are competitive and have commercial development value.

Keywords: Waste aluminum electrolytic solution; Recovery; α-Al_2O_3; Materialization

1. Introduction

With the characteristics of a high capacity, resistance to medium and high voltage, and low unit prices, aluminum electrolytic capacitors are widely used in computer power supply units and motherboards [1]. The process materials involved in such capacitors include anode formed foil, electrolytic paper soaked in an electrolyte, cathode aluminum foil, guide pins, and an aluminum shell [2]. The anode and cathode aluminum foil is an especially critical material for aluminum electrolytic capacitors, and accounts for 40 and 8% of the material costs, respectively [3]. A galvanic corrosion or chemical etching method is generally adopted to convert high-purity aluminum foil (>99.98%) to anodic galvanic-corrosion or cathode etched aluminum foil, as this procedure can increase the surface area and relative capacity of the foil [4]. Subsequently, through a chemical procedure, anodic galvanic-corrosion and cathode etched aluminum foil become anode and cathode aluminum foil. The aluminum layer of anode aluminum foil is used as the anode of an aluminum electrolytic capacitor, and the aluminum oxide layer is used as the dielectric layer of

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the electrolytic capacitor [4]. The aluminum layer of cathode aluminum foil is used as the cathodic electrolyte of the aluminum electrolytic capacitor that is connected to external circuits. The aluminum oxide layer provides the aluminum electrolytic capacitor with a protection function when momentary reverse voltage occurs because of voltage instability, thus extending the life of the electrolytic capacitor. Fig. 1 shows the manufacturing process for capacitors. This shows that 32% hydrochloric acid is diluted to 10% hydrochloric acid, and high-purity aluminum undergoes electrolysis, during which 1.2 N waste hydrochloric acid and 12–15 g/L aluminum ions are produced. Production lines can currently produce 12 tons of aluminum from 25 tons of aluminum foil per month.

Previous studies have focused on the synthesis pathway of nano aluminum oxide, aluminum material sources, and how to control the average particle size and pattern, as well as the crystalline phase, to enhance aluminum purity and prevent pollution [5–8]. The degree of crystallinity of γ-alumina is highly affected by the aging process, and the phase transformation from gibbsite to gamma-alumina has been started at low temperature (≤200˚C), with highly crystalline γ-alumina obtained at 1,000˚C [8]. The

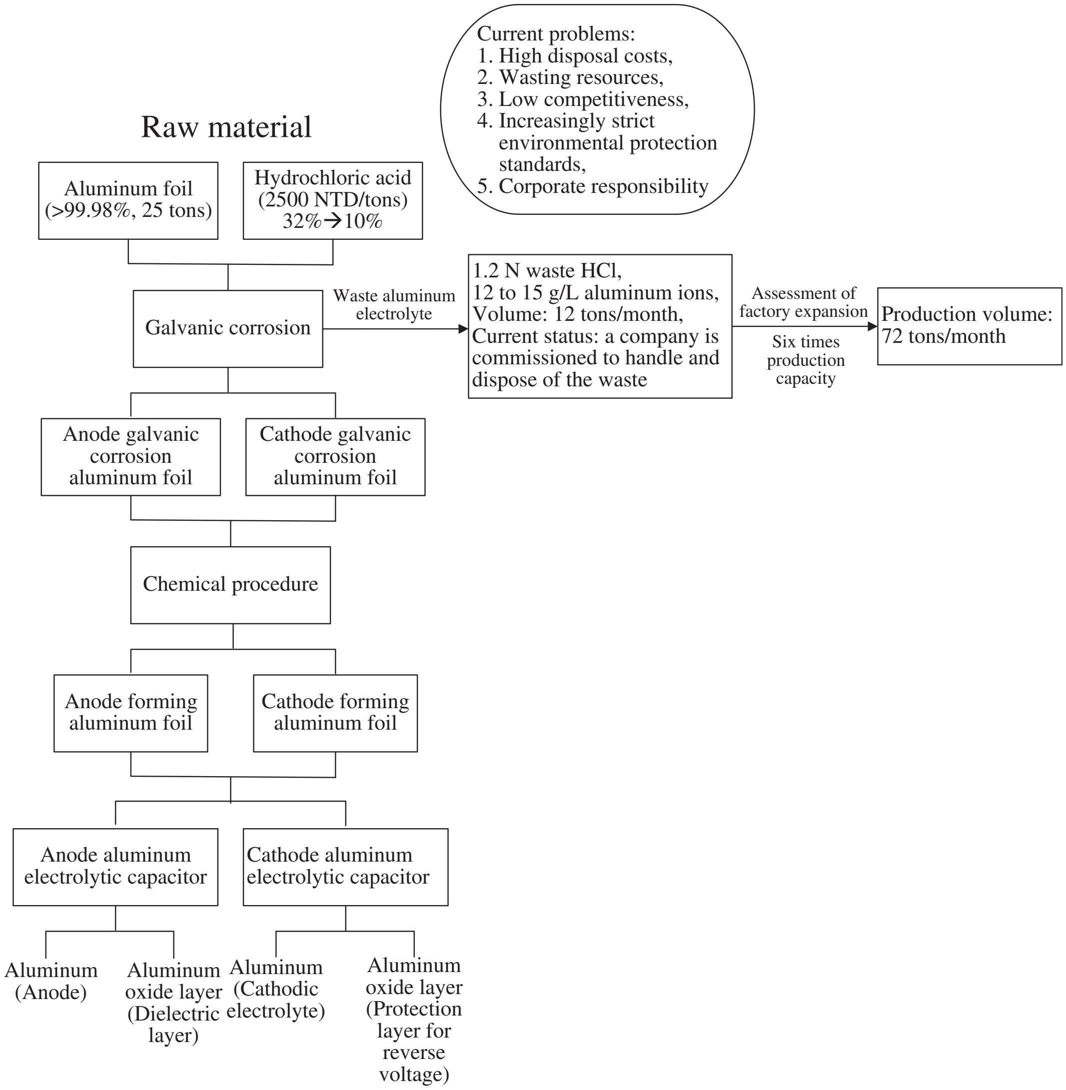


Fig. 1. The manufacturing process and current problems for capacitors.

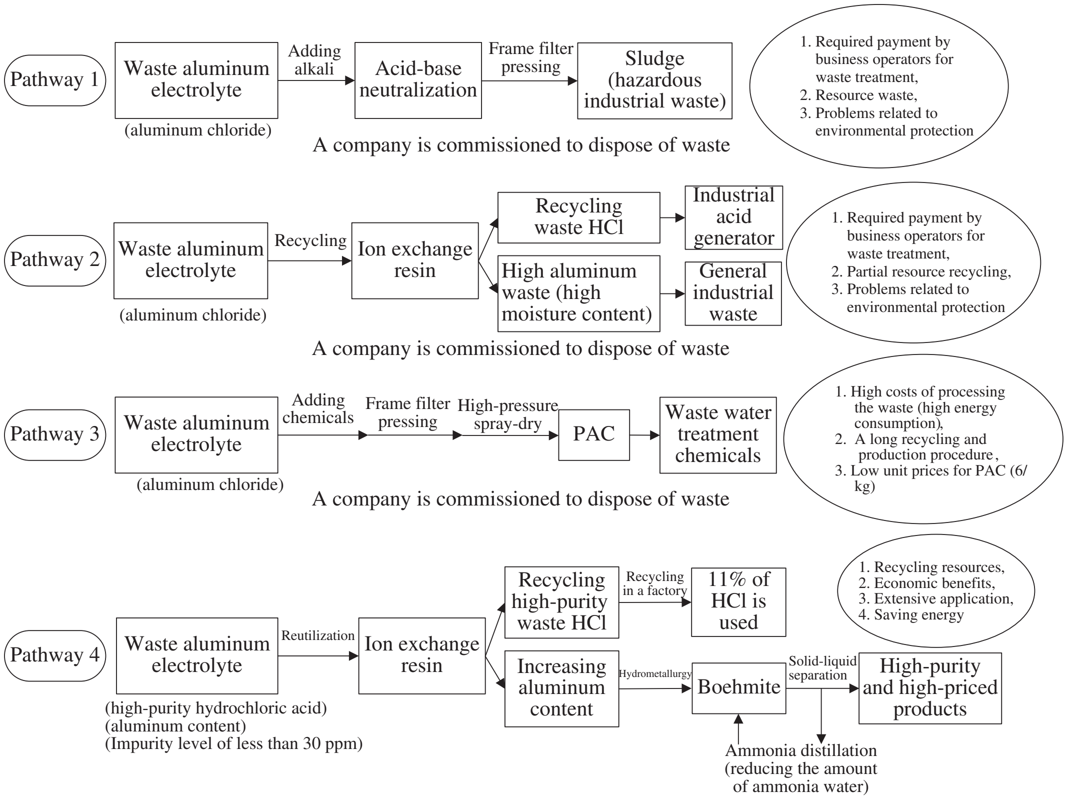


Fig. 2. Four pathways for processing waste aluminum electrolyte.

molecular characterization of aluminum hydroxy-gels derived from chloride and sulfate salts has been compared in an earlier study [9]. Additionally, the specific capacitance of the aluminum electrolytic capacitor is influenced by the concentration of HCl, current density, time, and temperature [10]. Hydrous aluminum oxide could thus be prepared by the reaction of aluminum salts and strong ammonia solution (with a pH of 9–10 to obtain precipitates). The precipitates then underwent aging, water washing, and filtration processes to completely remove anions (Cl^- or SO_4^{2-}) and NH_4^+ and obtain a filter cake. The filter cake was placed into a beaker, and ionized water and polyethylene glycol were added to this; the mixture was then vigorously stirred to thoroughly disperse the filter cake. The resulting powder was processed at high temperature to obtain superfine aluminum oxide powder. Under alkaline conditions, the AlO(OH) solution was in a supersaturated state, facilitating the reduction of the Gibbs free energy of the AlO(OH) particles in a hydrothermal reaction solution, increasing driving force, and forming nuclei [11]. Gibbsite was also used to produce α-Al_2O_3 powder with a particle size smaller than 150 nm [12]. However, to date no studies have examined the recovery of waste aluminum salts to fabricate nano aluminum oxide powder (α-Al_2O_3). Four pathways for processing waste aluminum electrolyte are summarized in Fig. 2, and detailed below.

Pathway 1: A company is commissioned to add alkali to waste aluminum electrolyte, which undergoes frame filter pressing to form general industrial waste sludge.

Pathway 2: Ion exchange resin is applied to waste aluminum electrolyte to recycle waste hydrochloric acid that can be used in a traditional acid generator [13]; high aluminum waste is general industrial waste, and a company is commissioned to dispose of the waste.

Pathway 3: A company is commissioned to add chemicals to waste aluminum electrolyte and use frame filter pressing and spray dry methods that consume a large amount of time and energy to form polyaluminum chloride (PAC) powder that can be used as an inexpensive water treatment chemical.

Pathway 4: Only 8–60 ppm impurities are contained in the waste aluminum electrolyte produced in a factory. A co-precipitation technique is adopted, and ammonia is added to the waste aluminum electrolyte to adjust the pH value to be greater than 9, thus producing white colloidal precipitates and an exothermic reaction. The stirring speed is 400 rpm, and the response time is 180–240 min. After solid–liquid separation, through an ammonia distillation system (an ammonia distillation tower heating and cooling procedure), ammonia is recycled, with the aim of reducing the amount of ammonia agents. After colloidal substances are dried, a boehmite (γ-AlO(OH)) forms. The boehmite is sintered at 1,200℃ for 2 h to produce high-purity corundum (α-Al_2O_3) powder.

The application methods (Pathway 4) are as follows: (1) sell 3 N aluminum oxide powders, (2) produce high-end transparent sapphire aluminum oxide, (3) prepare ceramic substrates, (4) produce a honeycomb catalyst, (5) produce a ceramic filter, and (6) create an exhaust gas purification device. Fig. 3 shows various transformations of aluminum oxide and explains the synthesis of high-purity aluminum oxide powder (adapted from Ref. [14]). Regarding the technique used in this study, the transformation sequence of boehmite is fast and stable, and the operating procedure is simple. This study thus develops an effective method to recycle the waste aluminum electrolytic solution generated from the manufacturing of capacitors, reduce the costs of producing nano aluminum oxide, and dispose of industrial waste. The anion-exchange resin and aging reaction are used to recover nano-Al_2O_3. The particle size, elemental compositions, and morphologies of recovered product are analyzed by a laser diffraction particle size analyzer (LS), X-ray fluorescence analyzer (XRF), X-ray diffraction analyzer (XRD), and scanning electron microscopy (SEM), respectively. The recovery rates of hydrochloric acid (HCl) and ammonia are also analyzed.

2. Materials and methods

2.1. Materials

Waste aluminum electrolyte was obtained from a factory that produces solid-aluminum electrolytic capacitors. The factory also manufactures electronic components and produces aluminum and cathode foil, particularly for low-voltage and solid capacitors. The factory has the largest production capacity in Taiwan, and it has 14% of the global market. At present an outside company is commissioned to dispose of the waste aluminum electrolyte, but this method not only imposes high costs on the business operators, but also

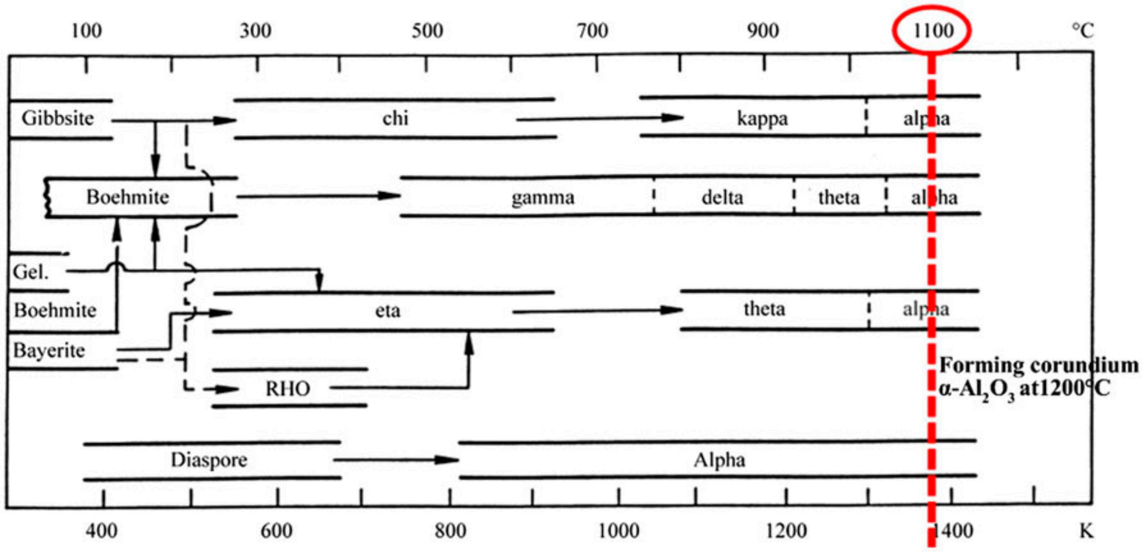


Fig. 3. Thermal transformation sequence of the aluminum hydroxides (adapted from Ref. [14]).

wastes resources. It is thus desirable that the waste aluminum electrolyte be recycled to minimize the environmental impacts.

All chemicals used in this study were analytical grade reagents and obtained from commercial sources. All aqueous solutions were prepared with de-ionized water.

2.2. Methods

The recycling of waste hydrochloric acid electrolyte and recovery of aluminum are assessed in this work, with anion-exchange resin being used to recycle the waste hydrochloric acid electrolyte. A batch processing method was adopted. Three liters of waste aluminum electrolyte was processed by a peristaltic pump each time, and the inflow velocity was about 50–600 ml/min. The recycling rate of waste hydrochloric acid was analyzed using an ion chromatography analyzer.

After recycling of the waste hydrochloric acid, the co-precipitation (mineralization crystallization) technique was employed to prepare high-purity boehmite (AlO(OH)). Specifically, ammonia was added into the waste electrolyte solution to form boehmite. To reduce the use of chemicals and the cost of resource recycling, an ammonia distillation system was employed to separate ammonia from the filtrate through heating and cooling procedures after the solid–liquid separation of the wet boehmite reaction. Firstly, the ammonia was slowly added to the aluminum chloride, and then the pH of the solution was adjusted to 9.5 to form white colloidal precipitates. The stirring speed and aging reaction time were 400 rpm and 200 min, respectively. After solid–liquid separation, the ammonia distillation system was used to separate ammonia from the filtrate, so that the ammonia could then be reused. A 2 L flask with four necks was used as the reaction tank. The pH value of the solution was controlled between 8.78 and 9.38. The pressure and heating temperature of the reaction tank were controlled at 1 atm and 80–95˚C. The reaction time for ammonia distillation was 70–205 min. A condenser was employed to control the water flow and keep the condensing temperature inside the ammonia water recycling tank at less than 37˚C (i.e. room temperature). Because of the lack of condensation under reduced pressure, the difference in concentration levels (wt%) between the periods before and after recycling was analyzed, and the recycling rate was calculated.

Residue solids were washed at least three times by de-ionized water and absolute alcohol (the solution was stirred for 10 min), and dried at 105˚C to form boehmite (α-AlO(OH)) (Sample A). Finally, the boehmite was sintered at 1,200˚C for 2 h to change the crystalline phase and to obtain aluminum oxide fine powder (α-Al_2O_3) (Sample B). The entire process, including preparing the boehmite and forming aluminum oxide powder, is shown in Fig. 4. The recovered product was characterized using an LS particle size analyzer (Beckman LS 230), XRF (Spectro Xepos), XRD (Shimadzu XRD-6100), and SEM (JEOL JSM-5610 LV). The purity of the recovered product was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista-MPX). The recovered products were also compared with commercial high-purity nanoscale aluminum oxide powder (Sample C).

3. Results and discussion

3.1. HCl and ammonia recovery

The commonly used method of lime neutralization of the acid content and precipitation of the metal content from waste pickle liquor leads to the loss of acid and metal values, along with the generation of a huge amount of sludge that is objectionable due to the problem that disposal of this presents [13]. The recycling/recovery/reuse of waste pickle liquor is carried out to convert this material into a secondary source of acid and metal content [13]. Hydrochloric acid was recovered from the waste aluminum electrolyte through anion exchange resin selectivity. The recycling

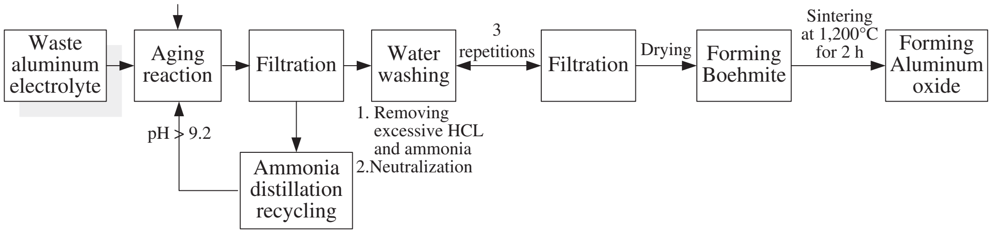


Fig. 4. The procedure for reusing the high-purity aluminum oxide obtained from waste aluminum electrolyte.

Table 1
Recycling rate of waste hydrochloric acid after anion exchange resin

Run	Acidity of waste HCl (N)	Acidity following recycling (N)	Concentration of Al^{3+} in waste aluminum electrolyte (g/L)	Concentration of Al^{3+} following resin absorption (g/L)	Recycling rate of waste HCl (%)	Impurities (mg/L)
1	1.18	1.14	11	20	61	27
2	1.15	1.16	13	24	67	20
3	1.16	1.17	17	33	75	26
4	1.19	1.16	18	38	72	19
5	1.21	1.18	15	27	76	23
6	1.51	1.14	18	32	65	32
7	1.26	1.28	20	36	75	16
8	1.15	1.20	14	27	68	22
9	1.46	1.19	16	30	69	13
10	1.53	1.22	17	32	72	25

Table 2
Recycling rate of ammonia obtained using an ammonia distillation procedure

Run	pH of waste ammonia	Concentration of waste ammonia (wt%)	Heating temperature (℃)	Steam temperature (℃)	Inflow velocity (ml/min)	Steam flow (ml/min)	Concentration of recycled ammonia (wt%)	Reaction time (min)	Recycling rate of distilled ammonia (%)
1	8.78	3.58	80	102	28	12	20.45	70	63
2	8.87	3.25	83	105	30	15	21.52	102	67
3	9.17	3.56	89	103	33	13	23.76	135	73
4	9.38	3.47	92	105	38	16	23.92	156	76
5	9.09	3.58	93	102	27	13	24.15	175	80
6	8.80	3.56	88	103	31	15	18.10	96	54
7	9.23	3.70	85	102	36	14	23.88	83	77
8	9.11	3.29	90	101	36	12	23.64	205	75
9	8.89	3.81	90	103	34	11	20.29	167	63
10	9.05	3.65	95	105	38	15	24.86	123	82

rate of the waste hydrochloric acid used in the manufacturing process was greater than 61%, and the amount of impurities in the recycled hydrochloric acid was less than 32 mg/L (as shown in Table 1). The optimal recycling rate of recycled hydrochloric acid was 76%.

A previous study shows that aluminum oxide could be synthesized from the aluminum chloride by a co-precipitation technique (using ammonium hydroxide) [15]. However, to date no studies have reported on the recycling of ammonia. In this work, the ammonia was separated from the filtrate of waste electrolyte solution after the recycling of hydrochloric acid and the formation of boehmite. The recycling concentration of ammonia was 18.10–24.86 wt%, and the optimal recycling rate was 82% (as shown in Table 2). The reuse of waste hydrochloric acid and ammonia would thus not only reduce the chemical costs, but also reduce the disposal costs associated with waste aluminum electrolyte.

Table 3
XRF analysis of recycled products obtained from waste aluminum electrolyte

Element (mg/kg)	Sample A	Sample B	Sample C
Si	850	462	235
Cl	8,707	–	–
Ca	101.8	64.7	24
Sn	28.1	13.3	–
Fe	6.5	5.8	8.8
Ni	2.8	2.6	1.9
Ga	–	–	2.6

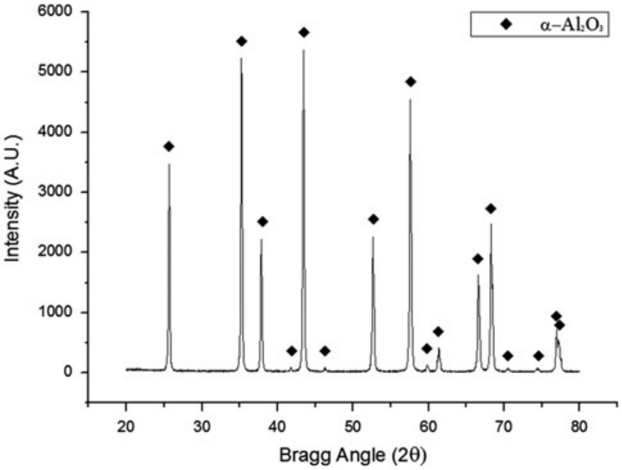


Fig. 5. XRD diffraction pattern of aluminum oxide synthesized using waste aluminum electrolyte.

3.2. *Nano-Al_2O_3—yield and product characterization*

Table 3 shows the results of the XRF analysis of recycled products obtained from waste aluminum electrolyte. Chlorine and silicon were the major impurities in the boehmite sample (A), due to the large amount of aluminum chloride in the waste aluminum electrolyte. The use of three repeated washing procedures can reduce the amount of impurities, and, in a later stage, after the aging reaction and the sintering procedure, the amounts of silicon, chlorine, and calcium in the aluminum oxide powder (B) were found to have decreased significantly. However, the amounts of the impurities of silicon, calcium, tin, and nickel in the recovered aluminum oxide powder (Sample B) were slightly higher than those seen in the commercial aluminum oxide powder (which has the characteristics of high price and purity) (Sample C).

The XRD diffraction pattern of Sample B is shown in Fig. 5. It can be seen that Sample B, obtained from recovered boehmite (Sample A) calcinated at 1,200˚C, presented the crystalline phase of α-Al_2O_3 and

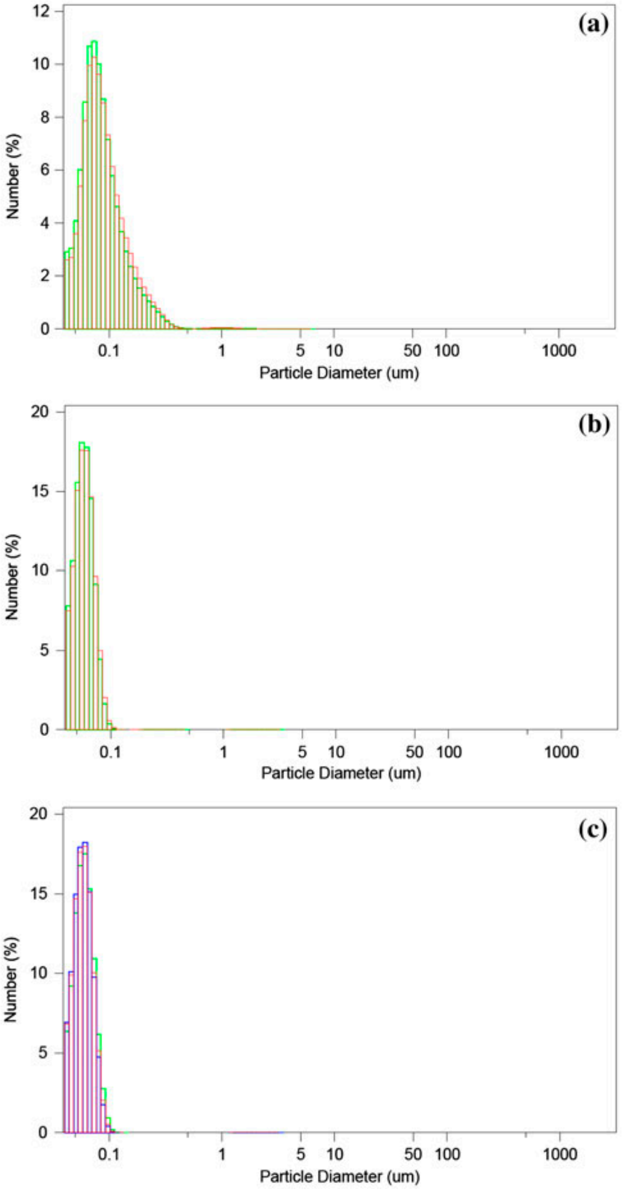
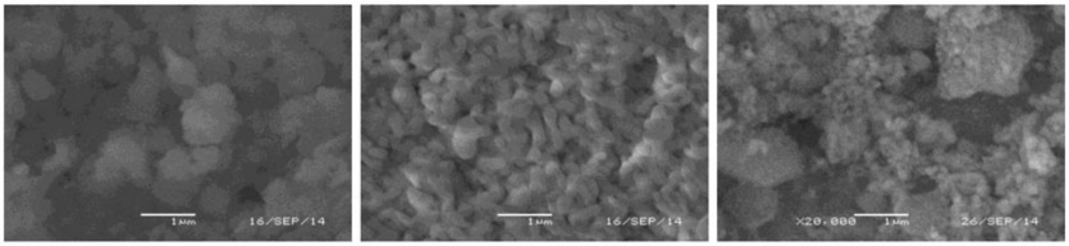


Fig. 7. LS particle size analysis of (a) boehmite and (b) aluminum oxide synthesized using waste aluminum electrolyte, and (c) commercially available high-purity aluminum oxide powder.



Sample A

Sample B

Sample C

Fig. 6. SEM morphologies of recycled products obtained from waste aluminum electrolyte.

Table 4
Purity analysis of recycled products obtained from waste aluminum electrolyte

Impurity (mg/kg)	Sample A	Sample B	Sample C
B	77.6	31.3	–
Fe	24.6	19.6	20.2
K	66.6	32.6	11.2
Na	19.5	24.8	16.1
Si	15.8	23.1	26.2
Sn	143.6	51.9	–
Ca	982.2	386.1	143.5
Zn	–	–	16.5
V	–	–	16.2
Purity (%)	99.867	99.943	99.975

matched with JCPDS 00-010-173. The XRD diffraction pattern of Sample B is similar to that seen with the synthesis of aluminum oxide from the aluminum chloride by co-precipitation technique [15]. Fig. 6 shows the SEM morphologies of boehmite (Sample A), recovered aluminum oxide powder (Sample B), and commercial aluminum oxide powder (Sample C) at 20 k magnification. The particles of Sample A were spherical; the particle size was greater than 1 μm. The particles of Sample B were spherical and agglomerated. A previous study shows that the synthesized α-Al_2O_3 nanomaterials are highly agglomerated [15]. The particle size of Sample C was substantially different from those of the other samples, and the particles were partially agglomerated. The small particles in Sample C were smaller than 100 nm.

Fig. 7 shows the results for the LS particle sizes of the recycled products obtained from waste aluminum electrolyte and commercially available high-purity nanoscale aluminum oxide powder. The average particle size of boehmite (Sample A) synthesized using waste aluminum electrolyte was 1.221 μm. At the later stage, after the aging reaction and phase transformation, the average particle size of aluminum oxide powder (Sample B) was 0.174 μm. Compared with commercially available high-purity nanoscale aluminum oxide powder (Sample C) (0.058 μm), the average particle size of Sample B was larger, and this is because the higher sintering temperature with the latter increases the degree of agglomeration.

Table 4 shows the results of the purity analysis for the recycled products obtained from waste aluminum electrolyte, as obtained with inductively coupled plasma optical emission spectroscopy. The purity of boehmite (Sample A) synthesized using waste aluminum electrolyte was 99.867%; the purity of aluminum oxide powder (Sample B) obtained through the aging reaction and phase transformation was 99.943%. Both Samples A and B thus met the requirement for 3-N purity. Compared with the purity of commercially available high-purity aluminum oxide powder (Sample C) (99.975%), the purity of Sample B was 0.032% lower. The hydrochloric acid, ammonia, and boehmite can thus be recycled from waste aluminum electrolyte through an ion exchange resin and mineralization crystallization technique, and this waste treatment procedure could aid in the development of better mold factories.

4. Conclusion

In this study, the aluminum chloride obtained from a waste aluminum electrolyte factory was purified to form high-purity nanoscale aluminum oxide powder that could be used as the precursor of transparent sapphire aluminum oxide. The optimal recycling rates of HCl and ammonia were 76 and 82%. The boehmite (γ-AlO(OH)) was sintered at 1,200°C for 2 h to form aluminum oxide (α-Al_2O_3). The average particle size of α-Al_2O_3 was 0.174 μm and the purity was 99.943%. The crystal form, purity, particle pattern, and particle size distribution of the aluminum oxide fine powder resembled the specifications of commercially available high-priced and high-purity aluminum oxide fine powder. The processing technology proposed in this work is thus feasible, and its application methods and economies of scale are competitive and have commercial development value.

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