APPLIED CHEMISTRY

Studies on the Electrochemical Preparation of Sb_2O_3

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The electrochemical preparation of antimony trioxide (Sb_2O_3) employing an antimony anode and a stainless steel cathode is described. The effects of different electrolytes, electrolyte concentration, pH, temperature, anode current density, different cathode materials, and different additives on current efficiency and purity for the preparation of antimony trioxide were studied. A maximum current efficiency of 99.2% was achieved corresponding to the energy consumption of 1.26 kWh·kg^{-1}.

Introduction

Metal oxides are used in a variety of applications. In general, cuprous oxide, mercuric oxide, and antimony oxide are utilized in paints and pigments, in manufacture of glasses, etc. to include specific properties.[1] Antimony oxide (Sb_2O_3) has wide applications as an effective catalyst, retardant, conductive material, functional filler, optical material, and high-efficiency flame-retardant synergist in plastics, paints, adhesives, and textile back coating.[2−4] In addition, Sb_2O_3 is also used in as a catalyst in the polyester industry and as a clarifying agent in optical glass, TV tubes, lighting (bulbs and tube lights), and crystal production.[5]

The world consumes nearly 30 000 metric tons/year of antimony trioxide. Antimony−antimony oxide electrodes are used for pH measurements.[6]

It has been reported that[7] antimony trioxide can be produced (i) by roasting antimony trisulfide, (ii) by burning antimony in air (or) oxygen, (iii) by alkaline hydrolysis of antimony halides, and (iv) by hydrolysis of antimony trisulfide with superheated steam. The sulfide can be oxidized to antimony(III) oxide (volatilizing roasting) or to antimony(IV) oxide (nonvolatilizing). Volatilizing roasting has the advantage that volatile Sb_2O_3 is produced selectively in a 98% yield and is separated from the residue, which contains precious metals in a recoverable form. The basic reaction is

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \qquad (1)$$

If too much oxygen is available, antimony(IV) oxide is formed:

$$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_4 + 3SO_2 \qquad (2)$$

Above 560 °C the rate of reaction doubles considerably. During roasting, antimony(IV) oxide can react with antimony(III) sulfide to give antimony(III) oxide:

$$Sb_2S_3 + 9Sb_2O_4 \rightarrow 10Sb_2O_3 + 3SO_2 \qquad (3)$$

It has been reported that it can also be prepared by vacuum evaporation method from slag containing antimony[8] and by hydrolysis−precipitation method.[9]

An electrochemical process for the preparation of Sb_2O_3 was scarce in the literature. The growth and reduction of anodic antimony trioxide films on antimony electrode in alkaline sulfide solutions have been investigated using potentiodynamic, galvanostatic, and potentiostatic techniques.[10] Hefny[11] studied the dissolution behavior of the anodic oxide films on antimony in different aqueous solutions by impedance and potential measurements. Wikstrom[12] studied the kinetic of the electrooxidation and reduction of antimony in alkaline solutions and also the electrodeposition of antimony from trivalent antimony on antimony. The mechanism of dissolution and corrosion of metals in alkaline solutions was reported.[13] Ammar and Saad[14] studied the anodic behavior of antimony in dilute acid solutions and kinetics of oxide growth. From the literature it is found that the electrochemical preparation of antimony trioxide by anodic dissolution of antimony has not so far been attempted. This paper presents the results of the study undertaken on the electrochemical preparation of antimony trioxide by anodic dissolution of antimony. To optimize the parametric conditions, the cells were operated at different electrolytes, concentrations, pHs, temperatures and anode current densities.

Materials and Methods

Cell Construction and Electrolysis. The electrolytic cell (Figure 1) consisted of a 0.60-L glass vessel that was fitted with a poly(vinyl chloride) (PVC) cell cover with slots to introduce the electrodes, a pH sensor, a thermometer and the electrolytes. An antimony plate (surface area 0.0047 m^2, 99.99% purity; Alfa Aesar, U.K.) acted as the anode. The cathodes were stainless steel (SS 304; SAIL, India) sheets of the same size as the anode and placed on either side of the central anode at an interelectrode distance of 0.005 m. The cathodes were covered with a terelyne cloth. The temperature of the electrolyte was controlled to the desired value with a variation of ±2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. A regulated direct current (dc) was supplied from a rectifier (10 A, 0−25 V; Aplab model).

Electrolysis was carried out with different electrolytes such as ammonium nitrate, potassium nitrate, sodium nitrate, lithium nitrate, nitric acid, perchloric acid, sodium perchlorate, and sodium sulfate of 1 M concentration. All chemicals were of AnalaR grade (CDH, India), and a 0.5-L portion of solution

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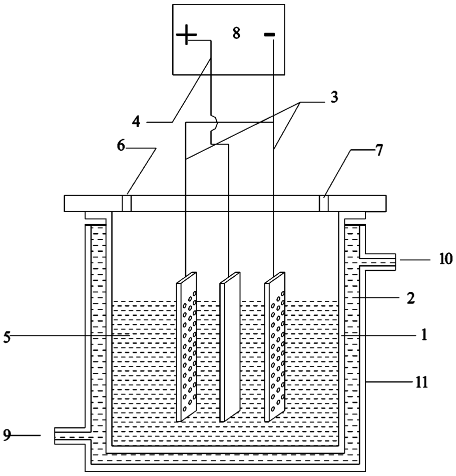

Figure 1. Laboratory scale cell assembly: 1, cell; 2, thermostatic water; 3, stainless steel cathode; 4, anode; 5, electrolyte; 6 and 7, holes to introduce pH sensor and thermometer; 8, dc source; 9, inlet; 10,outlet; 11, thermostat.

Table 1. Effect of Different Electrolytes on Current Efficiency for the Preparation of Antimony Trioxide[a]

no.	electrolyte	voltage (V)	current efficiency for Sb_2O_3 formation	energy consumption for Sb_2O_3 formation (kWh·kg^{-1})	purity of Sb_2O_3
1	NH_4NO_3	2.25	98.2	1.3	96.3
2	KNO_3	2.28	99.6	1.26	99
3	$NaNO_3$	2.26	98.5	1.31	98.7
4	$LiNO_3$	2.31	89.6	1.42	98.2
5	HNO_3	2.20	92	1.33	97.5
6	$HClO_4$				
7	$NaClO_4$				
8	Na_2SO_4				

[a] Conditions: electrolyte concentration, 1.0 M; electrolyte pH, 10.0; temperature, 333 K; volume, 0.5 L; anode, antimony; cathode, stainless steel; separator, terelyne cloth; current density, 3.0 A·dm^{-2}; quantity of charge passed, 2.0 A·h.

was used for each experiment. Current efficiencies were calculated as a function of experimental variations, such as different electrolytes, pH, and temperature; the concentrations of electrolytes were all analyzed using standard analytical procedures.[15]

Separation and Analysis of Antimony Trioxide. At the end of each experiment, the antimony trioxide collected at the bottom of the cell was filtered through a sintered crucible (Grade 4), washed thoroughly with distilled water, and dried in an air oven at 383 K for 2 h. The quantity of product formed was obtained by weighing the crucible before and after filtration. The purity of the product formed was estimated by iodimetry.[15]

The particle size distribution of Sb_2O_3 was determined by a laser diffraction particle sizer (Type 3600 E, Malvern, England). The crystal structure was studied using a JEOL X-ray diffractometer (JEOL, Japan).

Results and Discussion

Effects of Nature of Electrolyte. Table 1 shows the results of the experiments with various electrolytes such as NH_4NO_3, KNO_3, $NaNO_3$, $LiNO_3$, HNO_3, $HClO_4$, $NaClO_4$, and Na_2SO_4. Electrolytes such as $HClO_4$, $NaClO_4$, and Na_2SO_4 cause passivation of the anode, and the cell voltage continues to rise without the formation of solid Sb_2O_3. In the case of HNO_3, KNO_3, $NaNO_3$, and $LiNO_3$ electrolytes, the Sb_2O_3 formation is immediate and the solid Sb_2O_3 starts collecting at the bottom of the cell.

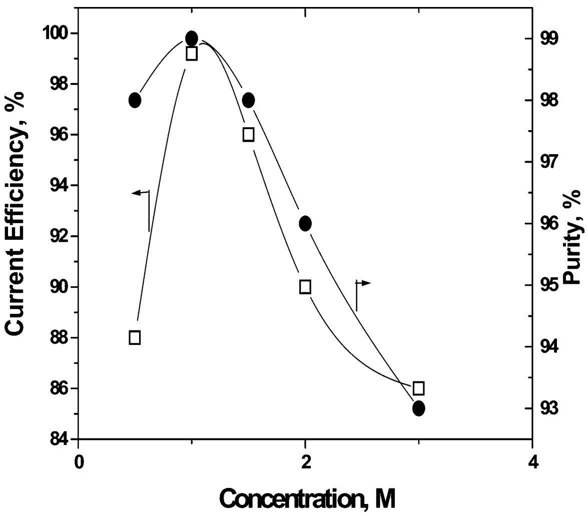

Figure 2. Variation of current efficiency and purity with KNO_3 concentration. Conditions: electrolyte, KNO_3; electrolyte pH, 10.0; temperature, 333 K; volume, 0.5 L; anode, antimony; cathode, stainless steel; separator, terelyne cloth; current density, 3.0 A·dm^{-2}; quantity of charge passed, 2.0 A·h.

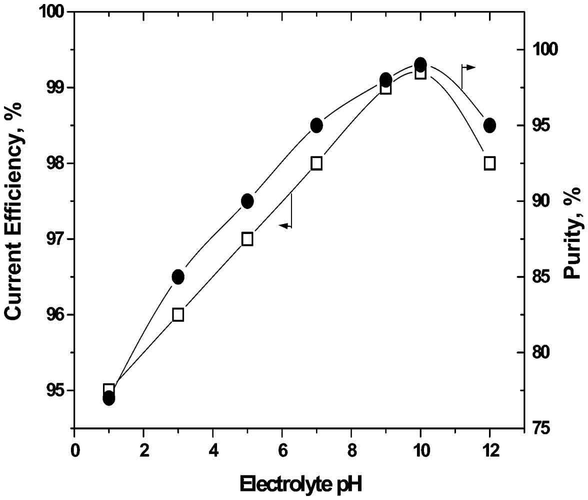

Figure 3. Variation of current efficiency and purity with electrolyte pH. Conditions: electrolyte, KNO_3; electrolyte concentration, 1.0 M; temperature, 333 K; volume, 0.5 L; anode, antimony; cathode, stainless steel; separator, terelyne cloth; current density, 3.0 A·dm^{-2}; quantity of charge passed, 2.0 A·h.

From the results it is found that, in the case of NH_4NO_3, KNO_3, $NaNO_3$, and HNO_3 electrolytes, the product obtained was of the same purity but the current efficiency seems to depend on the nature of the cation. Potassium nitrate yields a product of high purity combined with higher current efficiency. However, the nature of the cation does not seem to have any significant effect on the particle size of the product. Of the product, 90% has particle sizes below 17 μm with both KNO_3 and $NaNO_3$. Thus, for further studies KNO_3 was used as the electrolyte. Figure 2 shows the effects of the concentration of potassium nitrate on the current efficiency for the formation of antimony trioxide. The current efficiency shows a maximum at a concentration of 1.0 M. The current efficiency decreases significantly at higher concentrations. The decrease in current efficiency at higher concentrations is indicative of the fact that the rate of anodic dissolution is lower at higher nitrate concentrations. These results are in agreement with those obtained with phosphate electrolyte,[16] where the polarization curves have been found to be shifted to a less active direction of dissolution with increasing concentration. However, this effect does not seem to affect the purity very much, as found in Figure 2.

Effect of pH. The effect of pH on the current efficiency for the formation of antimony trioxide is shown in Figure 3. More active dissolution takes place at higher pH values and is fairly constant in the intermediate range.[17] It is observed that current efficiency increases steeply with temperature. According to a potential−pH diagram[18] antimony dissolves, forming various anionic species, such as SbO_3^-, SbO_2^-, $HSbO_2$, SbO^+, and Sb_2O_3. In addition to the above species, it forms SbH_3 at more negative potentials. The equilibrium potentials for the formations of these species are as follows.

$$\mathrm{Sb + H_2O = SbO^+ + 2H^+ + 3e^-} \qquad (E_o = 0.212 - 0.0394\mathrm{pH} + 0.0197 \log (\mathrm{SbO^+}) \quad (4)$$

$$\mathrm{Sb + 2H_2O = HSbO_2 + 3H^+ + 3e^-} \qquad (E_o = 0.230 - 0.0591\mathrm{pH} + 0.0197 \log (\mathrm{HSbO_2}) \quad (5)$$

$$\mathrm{Sb + 2H_2O = SbO_2 + 4H^+ + 3e^-} \qquad (E_o = 0.446 - 0.0788\mathrm{pH} + 0.0197 \log (\mathrm{SbO_2}) \quad (6)$$

$$\mathrm{Sb_2O_3 + 3H_2O = 2\,SbO_3^- + 6H^+ + e^-} \qquad (E_o = 0.794 - 0.0886\mathrm{pH} + 0.0295 \log (\mathrm{SbO_3^-}) \quad (7)$$

$$\mathrm{2SbO+ + 3H_2O = Sb_2O_5 + 6H^+ + 4e^-} \qquad (E_o = 0.581 - 0.0886\mathrm{pH} + 0.0295 \log (\mathrm{SbO^+}) \quad (8)$$

Depending on the pH and the solution concentration, the element can be oxidized to the trivalent state in the form of antimonyl cation SbO^+ and antimonous anhydride Sb_2O_3, which dissolves as antimonious acid $HSbO_2$ and antimonite, SbO_2^- or $Sb(OH)_4^-$. More vigorous oxidation by means of H_2O_2 etc., oxidizes it to the pentavalent state. Depending on the pH, the following substances can be formed: antimonic cations SbO_2^-, pentoxide Sb_2O_5, or antimonates SbO_3^-. Antimony trioxide has an amphoteric nature. In very acid media of pH from −2 to +1, it dissolves as antimonyl ions SbO^+. In solutions of pH from 2 to 10.4 the solubility of Sb_2O_3 is independent of the pH, which indicates the formation of an undissociated substance, $HSbO_2$.

The more negative peak potentials at pH 10 indicate the active dissolution of antimony in nitrate solutions.[16] This is true in the present case also, as higher current efficiency and purity were observed around pH 10. This potential region corresponds to the formation of $HSbO_2$ as per the pH−potential diagram. Hence, it can be presumed that Sb forms $Sb(OH)_{ads}$, which combines with OH^- ions initially forming $(SbO)_{ads}$ and finally $HSbO_2$ and Sb_2O_3.

The reaction scheme is as follows:[16]

$$\mathrm{Sb + OH^- = Sb(OH)_{ads} + e^-} \qquad (9)$$

$$\mathrm{Sb(OH)_{ads} + OH^- = (SbO)_{ads} + H_2O + e^-} \qquad (10)$$

$$\mathrm{(SbO)_{ads} + OH^- = HSbO_2 + e^-} \qquad (11)$$

$$\mathrm{(SbO)_{ads} + HSbO_2 + OH^- = Sb_2O_3 + H_2O + e^-} \qquad (12)$$

It has also been indicated that, under weak oxidizing conditions, in strong acid solutions Sb goes into solutions in the trivalent state as SbO^+.

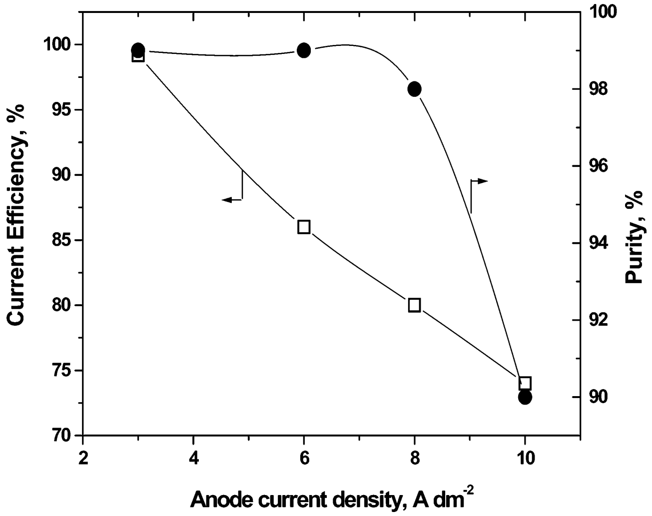

Figure 4. Variation of current efficiency and purity with anode current density. Conditions: electrolyte concentration, 1.0 M; electrolyte pH, 10.0; temperature, 333 K; volume, 0.5 L; anode, antimony; cathode, stainless steel; separator, terelyne cloth; quantity of charge passed, 2.0 A•h.

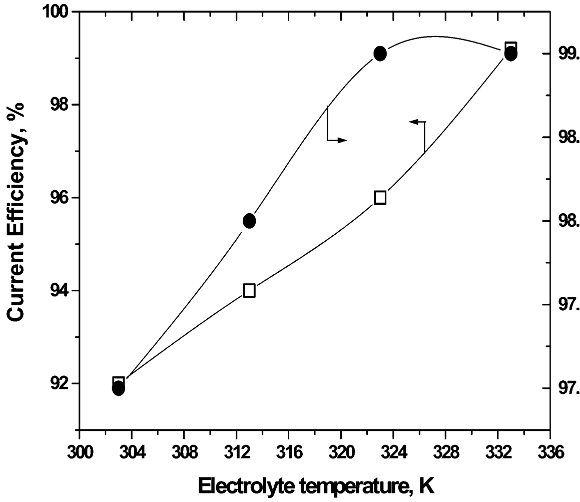

Figure 5. Variation of current efficiency and purity with electrolyte temperature. Conditions: electrolyte concentration, 1.0 M; electrolyte pH, 10.0; volume, 0.5 L; anode, antimony; cathode, stainless steel; separator, terelyne cloth; current density, 3.0 A•dm^{-2}; quantity of charge passed, 2.0 A•h.

The pH affects not only the current efficiency and purity but also the particle size. At pH 1.0 more than 50% of the product has sizes about 17 μm. As the pH increases, the particle size decreases. The particle size distribution is constant above pH 6.0, and the larger particles are practially very much less.

Effect of Anode Current Density. The anode current density markedly affects the current efficiency, as shown in Figure 4. Lower current densities show good current efficiency combined with high product purity. Higher anodic current density must increase the rate of electrodissolution of Sb anode. However, the continued increase would possibly cause a change in the mass transfer rate. That may result in the formation of soluble antimony nitrate. The uneven dissolution and large pits on the surface may be due to the above. This may also be a reason for the decrease in the purity at higher current densities, where the product contains metallic antimony as an impurity. The particle size (17 μm) distribution is uniform only at an intermediate current density of 3 A•dm^{-2}. It is found that larger (90 μm) particles have formed at higher current densities.

Effect of Temperature. Figure 5 shows the effect of temperature on the current efficiency and purity of Sb_2O_3

Table 2. Effect of Different Cathode Materials on Current Efficiency for the Preparation of Antimony Trioxide[a]

no.	cathode	voltage (V)	current efficiency for Sb_2O_3 formation	purity of Sb_2O_3
1	stainless steel	2.28	99.2	99
2	graphite	2.30	96.4	96.7
3	mild steel	2.30	87.4	97.7
4	antimony	2.54	99.6	90.8

[a] Conditions: electrolyte concentration, 1.0 M; electrolyte pH, 10.0; temperature, 333 K; volume, 0.5 L; anode, antimony; separator, terelyne cloth; current density, 3.0 A·dm^{-2}; quantity of charge passed, 2.0 A·h.

Table 3. Effect of Different Additives on Current Efficiency for the Preparation of Antimony Trioxide[a]

no.	additives	voltage (V)	current efficiency for Sb_2O_3 formation	purity of Sb_2O_3
1	nil	2.28	99.2	99
2	sodium gluconate	2.35	85.6	89.1
3	potassium dichromate	2.40	99.7	88.3
4	sodium citrate	2.31	99.5	98.8

[a] Conditions: electrolyte concentration, 1.0 M; electrolyte pH, 10.0; temperature, 333 K; volume, 0.5 L; anode, antimony; cathode, stainless steel; separator, terelyne cloth; current density, 3.0 A·dm^{-2}; quantity of charge passed, 2.0 A·h.

formation. It is observed that current efficiency increases steeply with temperature while the increase in purity is only marginal. Since Sb_2O_3 is formed by the reaction of $(SbO)_{ads}$ and hydroxylated SbO in the presence of OH^-, the reaction is almost equivalent to dehydration of SbO·OH species. At higher temperature this reaction rate may be faster, so current efficiency increases. Further, the formation of $(SbO)_{ads}$, which is the intermediate for the formation of Sb_2O_3, is dependent on the OH^- ion concentration at higher temperature; the increase in mass transfer must produce a corresponding increase in the current efficiency. Moreover, at lower temperatures higher potentials may be required for the formation of Sb_2O_3. Increasing the temperature may result in ease of removal of the oxide from the surface.

Effect of Cathode Materials. The effect of different cathode materials on current efficiency for the preparation of antimony trioxide is presented in Table 2. Except for mild steel, the other tested cathode materials such as stainless steel, graphite, and antimony show good current efficiencies. The purity of the product is the lowest with antimony cathode, due to the formation of surface hydrides, even though the current efficiency is the maximum. According to the Pourbaix diagram, surface hydrides of Sb are formed at higher cathode potentials. This has been observed earlier,[14] and in the present case also the formation of black coating on the cathode is considered as being due to some of the surface hydrides. In order to avoid this contamination, a terelyne cloth was used as a separator. Another advantage of the separator is to prevent the migration of Sb_2O_3 formed at the anode to the cathode and thereby maintain the purity at a higher level.

Effect of Additives. Sodium citrate, cetyltrimethylammonium bromide (CTAB), etc. have been used as stress relievers in the coating of PbO_2.[19] Similarly, in the preparation of antimony trioxide a few additives such as sodium gluconate, dichromate, and sodium citrate of 2 g/L were studied, and the results are presented in Table 3. Potassium dichromate prevents the formation of surface hydrides at the cathode,[20] but the purity is very much less and coloration of the product did not commend its use. Sodium gluconate has actually some negative effect since both current efficiency and purity are lower than without the additives. Sodium citrate shows an encouraging performance, and anodic dissolution has also been found to be uniform.

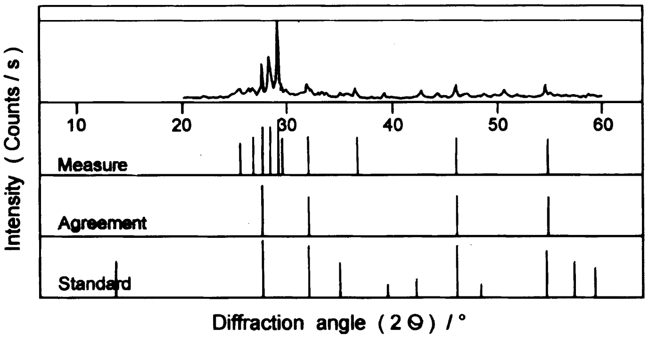

Figure 6. XRD diffractogram of electrolytic Sb_2O_3 at an electrolyte pH 1.0.

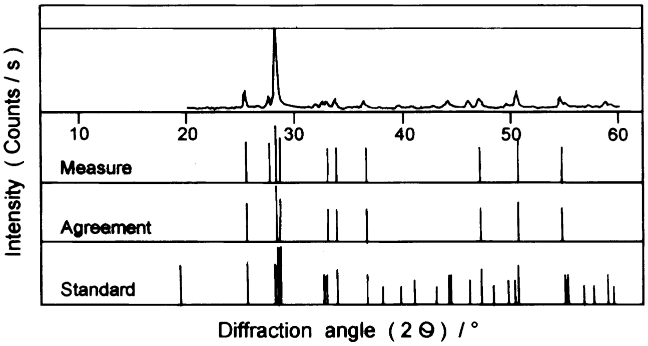

Figure 7. XRD diffractogram of electrolytic Sb_2O_3 at an electrolyte pH 10.0.

Figures 6 and 7 shows the X-ray diffraction (XRD) patterns obtained with the product antimony trioxide formed at pH 1.0 and 10.0, respectively. The study indicates that the crystal structure is affected by pH. Under highly acid conditions the crystallites are cubic, and above pH 10 they are orthorhombic. The effect of pH on crystal modification has been observed also in the case of PbO_2, where under acid conditions rutile structure (tetragonal) and in alkaline conditions orthorhombic structure have been observed.[21]

Conclusion

The electrochemical preparation of antimony trioxide (Sb_2O_3) can proceed efficiently, when 1.0 M $NaNO_3$ (pH 10) is electrolyzed using an antimony anode and a stainless steel cathode with an anode and cathode current density of 3 A dm^{-2}, with a diaphragm of terelyne cloth to achieve a current efficiency of 99.2% corresponding to an energy consumption of 1.26 kWh·kg^{-1}.

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