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Studies Relating to Electrolytic Preparation of Potassium Bromate

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The electrochemical preparation of potassium bromate ($KBrO_3$) from potassium bromide (KBr), using a noble-metal oxide coated titanium anode and a stainless steel cathode, is described. The effect of different anode materials, anode current density, pH, and temperature of the electrolyte on the current efficiency for the preparation of $KBrO_3$ was studied. A maximum current efficiency of 97% was achieved when 240 g/L of bromide (pH 6.0) is electrolyzed at an anode and cathode current density of 20.0 A/dm^2 and a temperature of 333 K.

Introduction

Bromates, especially alkali-metal bromates, have several important applications, the most important being their use as valuable oxidizing agents and brominating agents in analytical chemistry. Several chemical methods[1] have been suggested for the preparation of bromates; however, electrolytic preparation is, by far, the most elegant method. The preparation of bromate via the electrolysis of bromide (similar to that of chlorates) was studied by various authors.[2,3] The kinetics of electrolytic bromate formation in dilute bromide solutions (0.005−0.1 mol dm^{-3}) has been investigated.[4] Attempts were made to study different anode materials, such as graphite, carbon, lead dioxide, and lead peroxide. Graphite undergoes considerable wear, because of the oxidation of the binder material, resulting in the formation of carbon dioxide. Because of its disintegration, it not only contaminates the electrolyte but also increases the interelectrode distance during electrolysis, thereby increasing the cell voltage and, consequently, energy consumption in halate cells.[5−11] Lead dioxide and lead peroxide[12] were other anode materials studied for bromate preparation, because they have a higher conductivity than most metal oxides. The disadvantage of these electrodes was higher overvoltage for bromine evolution.

Because of the aforementioned disadvantages of the graphite, lead dioxide, and lead peroxide anodes, noble-metal oxide coated titanium anodes are being substituted. The advantages and important features of these are higher electronic conductivity and high chemical stability. The literature contains no publication that addresses the investigation on the preparation of bromates via the electrolysis of bromide at noble-metal oxide electrodes, and the only publication that relates to the mechanism of bromates by electrolysis was published by Cettou.[4] Now, an attempt has been made to prepare bromate using a noble-metal oxide coated titanium anode and a stainless steel cathode. To optimize the parametric conditions, the cells were operated at different anode materials, pH values, temperatures, and anode current densities.

Materials and Methods

Cell Construction and Electrolysis. The electrolytic cell (Figure 1) consisted of a 0.5-L glass vessel that was fitted with a poly(vinyl chloride) (PVC) cell cover with slots that allowed the electrodes, pH sensor, thermometer, and electrolytes to be introduced. A stainless steel (SS304, 99.8% pure, from SAIL, India) sheet (area of 0.006 m^2) was used as a cathode. Noble-metal oxide ($RuO_2/TiO_2/SnO_2$) coated titanium (0.006 m^2), 99.8% pure (Mithani (I) Limited, India), acted as anode with an interelectrode distance of 1.0 cm from the cathode. The mixed-oxide electrodes were prepared using the thermal decomposition process that has been described in the literature.[13] The coating solution for the preparation of the anodes was prepared from the chlorides of the three metals, viz, $RuCl_3 \cdot xH_2O$ (38.4% Ru) (Johnson Mathey, U.K.), $TiCl_4$ (25.1% Ti) (Riedel De Haan AG), and $SnCl_4 \cdot 5H_2O$ (33.9% Sn) (J.T. Baker Chemical Co., USA). The salts of the aforementioned three metals were taken in the ratio of 30 RuO_2/50 TiO_2/20 SnO_2, dissolved in isopropanol (Johnson Mathey, U.K.), and then painted over the pretreated titanium mesh (which was polished, degreased, and etched in a 10% oxalic acid (Johnson Mathey, U.K.) solution at 363 K for 30 min) to produce a uniformly spread layer. The paint layer was dried at 353 K in an air oven for 10 min to evaporate the solvent. The samples were then transferred to a muffle furnace that was maintained at 673 K for 10 min. During this period, the heating zone of the furnace was maintained with a good supply of air from a compressor. The electrode was then removed from the furnace and cooled. The process of brushing the coating solution, drying at 353 K, and then heating in the presence of air at 673 K was repeated for 6−8 times. After the final coating, the electrode was heated at 723 K for 1 h and allowed to cool in the oven itself over a period of 8 h. A regulated direct current was supplied from a

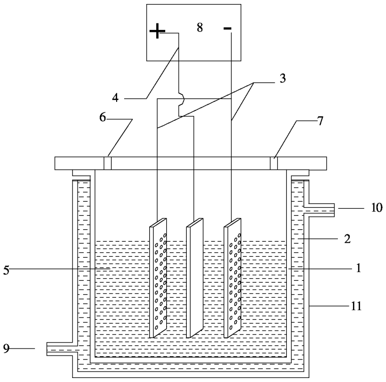

Figure 1. Laboratory scale cell assembly. Legend: 1, cell; 2, thermostatic water; 3, stainless steel cathode; 4, anode; 5, electrolyte; 6 and 7, holes to introduce the pH sensor and thermometer; 8, DC source; 9, inlet; 10, outlet; and 11, thermostat.

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Table 1. Effect of Different Anode Materials on the Current Efficiency for the Preparation of Potassium Bromate[a]

sample	anode	voltage (V)	current efficiency for $KBrO_3$ formation (%)	purity of $KBrO_3$ (%)
1	noble-metal oxide coated titanium	3.3	97.0	99.0
2	graphite	3.7	90.0	83.0
3	graphite substrate lead dioxide	3.9	96.0	98.0

[a] Conditions: electrolyte concentration, 240 g/L (as bromide); electrolyte pH, 8.0; temperature, 333 K; volume, 0.45 L; cathode, stainless steel; and current density, 20.0 A/dm^2.

rectifier (25 A, 0−25 V, Aplab Model). The lead dioxide anode with a graphite substrate was prepared by depositing lead dioxide at 65 °C from a lead nitrate bath, as described in the literature.[14]

Potassium bromide (KBr, laboratory reagent grade) was dissolved in distilled water until the desired concentration was attained; 0.45 L of solution was used for each experiment, which was used as an electrolyte. A quantity of sodium dichromate (2 g/L, from BDH, India) was added in the electrolyte to prevent the cathodic reduction. The electrolyte pH was monitored using a pH probe and was regulated by adding either an acid or a base. Each experiment was continued until the theoretical charge had been passed and the cumulative current efficiency was calculated for each experiment. The effect of various parameters on current efficiency was determined.

Analysis. (a) Bromide. The bromide content was estimated using a standard silver nitrate (Analar Grade, Ranbaxy, India) solution and Rosin (Analar Grade, BDH, India) as an indicator.[15]

(b) Bromate. The bromate content was estimated using a standard thiosulfate (Analar Grade, BDH, India) solution and starch as an indicator.[15]

Results and Discussion

During the electrolytic oxidation of bromide solution to obtain bromate, the primary products of the electrode reactions are bromine and alkali, which react in the bulk electrolyte between the electrodes to form hypobromous acid and hypobromite. These subsequently react chemically to form bromate.[3]

The main reactions in the bromate electrolysis process can thus be written as follows. At the anode, bromine is formed:

$$2Br^- \rightarrow Br_2 + 2e^- \qquad (1)$$

At the cathode, hydroxyl ions and hydrogen are formed:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (2)$$

At the bulk, Br^- ions that are formed at the anode react rapidly with water to form hypobromous acid:

$$Br_2 + H_2O \rightarrow HBrO + H^+ + Br^- \qquad (3)$$

Because the electrodes are close together and have no diaphragm, the Br^- species can react with the hydroxyl (OH^-) ions that are formed at the cathode to produce hypobromite ions:

$$Br_2 + 2OH^- \rightarrow OBr^- + Br^- + H_2O \qquad (4)$$

As a result, the solution around the anode becomes strongly acidic and the solution in contact with the cathode is alkaline. In addition to this pH gradient, the concentration of hypobromous acid also establishes a gradient relatively high around the anode and relatively low around the cathode.

It is usually assumed that bromate is formed via the reaction of a hypobromite ion by a free hypobromous acid (reaction 5) when pH is 8.0−8.5. However when the pH is slightly alkaline, the electrochemical formation of bromate through discharge of the hypobromite ion at a potential equal to that for discharge of the bromide ion (reaction 6).

$$2HOBr + BrO^- \rightarrow BrO_3{}^- + 2H^+ + 2Br^- \qquad (5)$$

$$6BrO^- + 3H_2O \rightarrow 2BrO_3{}^- + 6H^+ + 4Br^- + 1.5O_2 + 6e \qquad (6)$$

According to reactions 5 and 6, bromate may be formed in two ways: either via a purely chemical reaction of the hypobromite ion with hypobromous acid in the bulk solution (chemical bromate formation) or via electrochemical oxidation of the hypobromite at the anode under simultaneous oxygen evolution (anodic bromate formation). If all bromate is formed by the chemical reaction 5, 6 Faradays are consumed in the oxidation of one mole bromide to bromate. This is said to correspond to a maximum current efficiency of 100%. If all bromate is formed by reaction 6, the current efficiency cannot be higher than 66.5% since one-third of the current is used for the evolution of oxygen. In other words, reaction 6 can be considered to be an anodic loss reaction. It has been established that reaction 5 is more plausible than by reaction 6.[3] The most favorable operating conditions for reaction 5 are a temperature of 333 with a pH of 8.0 − 8.5. The conditions for the formation of bromate through reaction 5 is exist in the present case also.

Effect of Anode Material. Table 1 shows that the current efficiency for the formation of potassium bromate ($KBrO_3$) with noble-metal oxide coated titanium anode is higher than that of graphite anode, in view of the catalytic nature of the metal-oxide-coated anode with low bromine overpotential. Not much variation was observed in the case of the lead dioxide anode. In addition, graphite anodes possess very limited service life (6−24 months; 15−25 kg graphite loss/ton of halates),[2] because they disintegrate during the electrolysis, because of the electrochemical oxidation of binding material and partially physical wear due to turbulent conditions at the anode surface. In the case of lead dioxide anode, the cell voltage was higher than that of the metal-oxide-coated anode, because of the higher bromine overpotential. Therefore, to overcome the disadvantages of graphite and lead dioxide anodes, the further experiments were performed with metal-oxide-coated titanium was used as an anode.

Effect of pH. The formation of bromate is dependent on the pH of the electrolyte, and it is found that if the solution is made more alkaline or acidic, the current efficiency falls off quickly.[4,12] When the electrolysis of an aqueous solution of bromide is performed, initially, the discharge of Br_2 and OH^- ions occurs, according to reactions 1 and 2: each of them may be discharged to a greater or lesser degree, depending on the electrolysis conditions. In a more-alkaline medium there is a predominant discharge of (OH^-) ion, thereby favoring the formation of free oxygen and in acid medium, it is favorable for the liberation of gaseous bromine by the discharge of bromide ions. Table 2 shows the variation of current efficiency with four different electrolyte pHs for the preparation of $KBrO_3$. From the table, it is evident that the higher current efficiency is observed at a

Table 2. Effect of pH on the Current Efficiency for the Preparation of Potassium Bromate[a]

sample	electrolyte pH	voltage (V)	current efficiency for $KBrO_3$ formation (%)	purity of $KBrO_3$ (%)
1	4.0	3.3	84.0	97.0
2	6.0	3.7	90.0	98.0
3	8.0	3.3	97.0	99.0
4	10.0	3.5	88.0	94.0

[a] Conditions: electrolyte concentration, 240 g/L (as bromide); temperature, 333 K; volume, 0.45 L; cathode, stainless steel; and current density, 20.0 A/dm^2.

Table 3. Effect of Anode Current Density on the Current Efficiency for the Preparation of Potassium Bromate[a]

sample	anode current density (A/dm^2)	voltage (V)	current efficiency for $KBrO_3$ formation (%)	purity of $KBrO_3$ (%)
1	10.0	2.8	95.0	99.0
2	20.0	3.3	97.0	99.0
3	30.0	4.0	97.0	98.0
4	40.0	4.8	98.0	98.0

[a] Conditions: electrolyte concentration, 240 g/L (as bromide); electrolyte pH, 8.0; temperature, 333 K; volume, 0.45 L; and cathode: stainless steel.

narrow pH value (~8.0). The results indicate that the increase in electrolyte pH from 4.0 to 8.0, increases the current efficiency from 84% to 97% for the preparation of potassium $KBrO_3$. Below pH 4.0, a shift in the $HOBr/OBr^-$ ratio to below 2:1, which is not ideal for the preparation of bromate. The excess hypobromite can either be decomposed or oxidized at the anode to produce oxygen and bromine, resulting in the fall of current efficiency at lower pH values. From the results, it is evident that the loss of bromine and oxygen increase at lower or higher pH values than at optimum value (i.e., pH 8.0).

Effect of Anode Current Density. The results of the influence of anode current density on current efficiency are shown in Table 3, which clearly indicate that the current efficiency increases with increasing anode current density. This is consistent with the results reported earlier.[3,4,12] However, the internal resistance (IR) drop increases linearly with the current density resulting in increase of cell voltage and consequently higher energy consumption. Hence, a compromise must be determined in selecting the current density for further investigation. It was thus maintained at 20.0 A/dm^2 for subsequent experiments.

Effect of Temperaure. The temperature effect of the bromate producing system is confined by a certain number of kinetic parameters encompassed by the relationship for current efficiency.[16] In addition, it is well-known that an increase of temperature decreases the cell voltage thereby resulting in the energy reduction. The most important effect of temperature for the process would be to increase the rate of the chemical conversion of the active bromine. In the present case, from the economical point view, a rather compromised temperature range of ~333 K can be maintained in the bromate cells with metal oxide coated titanium anode. Another important reason for limiting the temperature of the chlorate-producing system is due to the thermal decomposition of the hypobromous species, resulting in the evolution of oxygen.

Table 4. Effect of Temperature on the Current Efficiency for the Preparation of Potassium Bromate[a]

sample	electrolyte temperature (K)	voltage (V)	current efficiency for $KBrO_3$ formation (%)	purity of $KBrO_3$ (%)
1	313	4.0	92.0	99.0
2	323	3.7	95.0	99.0
3	333	3.3	97.0	99.0

[a] Conditions: electrolyte concentration: 240 g/L (as bromide); electrolyte pH, 8.0; volume, 0.45 L; cathode, stainless steel; and current density, 20.0 A/dm^2.

The result on the effect of temperature on the preparation of $KBrO_3$ is presented in Table 4. The table clearly shows that the current efficiency for the formation of potassium bromate increases with increasing temperature of the electrolyte. The current efficiency for the formation of $KBrO_3$ increases from 92% to 97% for the increase in temperature from 313 K to 333 K. This increase in current efficiency at higher temperatures is attributed to an increase in the rate of chemical conversion of the active bromine to bromate.[3] In the chlorate process, the cathodic reduction of intermediately formed hypochlorite ions is prevented by means of the addition of chromates to the electrolyte.[17,18] While Tilak[19] found that the reduction of hypochlorite and chlorate was completely suppressed on a stainless steel cathode and avoided the current efficiency loss. Hence, in the present instance also, the stainless steel cathode has been used for all experiments.

Conclusion

The electrochemical oxidation of potassium bromide (KBr) to potassium bromate ($KBrO_3$) on noble-metal oxide coated electrodes proceeds efficiently, (by achieving a current efficiency of 97%) when 240 g/L of bromide (pH 6.0) is electrolyzed at an anode and cathode current density of 20.0 A/dm^2 and a temperature of 333 K.

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