Chinese Chemical Letters Vol. 15, No. 12, pp 1487-1490, 2004

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Selection of Anodic Material Used in Electrolytic Process for Producing Hypophosphorous Acid

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Abstract: Black lead, Ti-Ru and Ti-PbO_2 were used as anode and stainless steel was used as cathode. The electrolytic process of producing hypophosphorous acid with four-compartment electrodialytic cell was studied. The comparison of some factors, such as anodic voltage, product concentration and current efficiency, of black lead, Ti-Ru, and Ti-PbO_2 electrodes was conducted. As a result, the Ti-PbO_2 electrode is the optimal anode material used, it can be in electrolytic process for producing hypophosphorous acid.

Keywords: Hypophosphorous acid, electrolysis, anodic material.

There are some references in abroad and in China. Sodium hypophosphite was used as raw material to produce hypophosphorous acid by electrolysis [1-6]. According to the patents and literatures reported, Ti-Ru electrode and black lead electrode have been used as anode in electrolytic process for producing hypophosphorous acid. Ti-Ru electrode cannot be applied widely in industry due to high cost and scarce resource of ruthenium in China. Although black lead anode is much cheaper, the application of black lead anode is limited because of following shortcomings: short lifetime, severely environmental pollution, and affecting the permeated capability of membrane. Therefore, it is very important to search new anodic material used for electrolytic process of producing hypophosphorous acid. Based upon correlative information[7], Ti-PbO_2 electrode, cheaper than Ti-Ru electrode, was selected as the anode. In this paper, the performances of black lead electrode, Ti-PbO_2 electrode and Ti-Ru electrode were compared and discussed.

The experimental apparatus is a four-compartment electrodialytic cell shown in **Figure 1**.

When a direct current flowed through the electrodialytic cell, the water was decomposed, and generated hydrogen ions in anodic compartment. The hydrogen ions transported from anodic compartment to product compartment through cationic exchange membrane (C) nder the action of electric field force. The anionic exchange membrane (A) isted cation diffusion and retained the hydrogen ions in product compartment. The material compartment started with a concentrated solution of sodium hypophosphite. The hypophosphite ions transferred through anionic exchange membrane from material compartment to product compartment under the action of electric field force. The

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cationic exchange membrane resisted anion diffusion and retained the hypophosphite ions in product compartment. As a result, the hypophosphite ions were combined with hydrogen ions forming hypophosphorous acid solution in the product compartment. Because of the cationic exchange membrane resistant, the hypophosphite ions did not enter into anodic compartment so as not to contact with oxygen liberated from anode, therefore the hypophosphite ions did not be oxidized. The following equations are reactions in anodic compartment, product compartment and cathodic compartment, respectively.

Anodic compartment : $2H_2O = 4H^+ + O_2\uparrow + 4e$

Product compartment: $H^+ + H_2PO_2^- = H_3PO_2$

Cathodic compartment: $2H_2O + 2e = 2OH^- + H_2\uparrow$

$Na^+ + OH^- = NaOH$

The reagents and preliminary concentration of various compartment electrolyte are as follows: 10 g/L sulfuric acid (anolyte), 10 g/L hypophosphorous acid (product compartment), 400 g/L hypophosphite sodium solution (material compartment), 10 g/L sodium hydroxide (catholyte). The black lead, Ti-PbO_2, and Ti-Ru electrodes are custom-made.

Black lead, Ti-PbO_2, and Ti-Ru were used as anodes and stainless steel was used as cathode. The electrodialytic cell ran for three hours. The electrode area was 40 cm^2 and current density was 30 mA/cm^2. To make sure the penetrability and lifetime of the ion exchange membranes, the electrolyte temperature was kept below 40℃ by using the cooling devices. Saturated calomel electrode was inserted into the anolyte as a reference electrode, keeping the constant distance between saturated calomel electrode and anode. During the electrolyzing, the anodic voltage between reference electrode and anode was measured continuously with potentiometer. The variation of anodic voltage with run time is shown in **Figure 2**

Figure 1 The four compartments electrodialytic cell

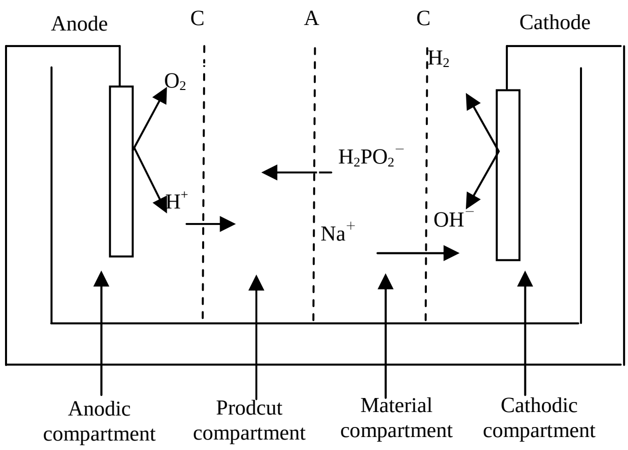


Figure 2 Variation of anodic voltage with run time

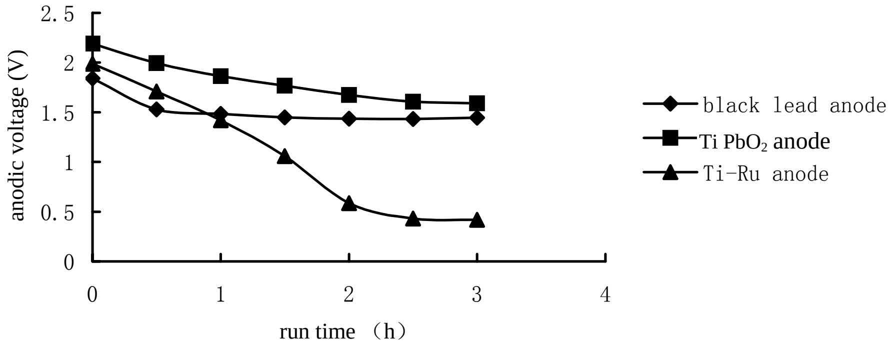


Figure 3 Variation of product (hypophosphorous acid) concentration with run time

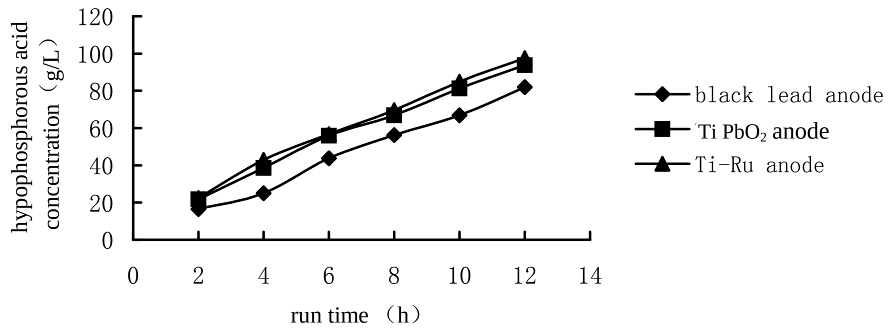
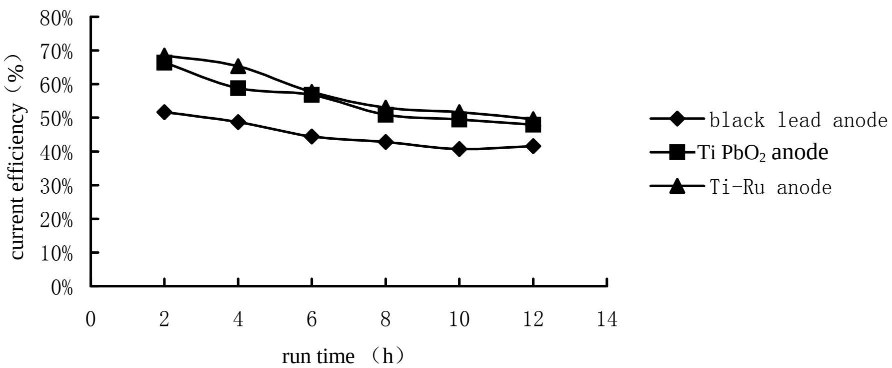


Figure 4 Variation of current efficiency of product compartment with run time



After 3 hours, the anodic voltages of black lead electrode, Ti-PbO_2 electrode and Ti-Ru electrode decreased from 1.839 V, 2.19 V and 1.99 V to 1.444 V, 1.589 V and 0.418 V, respectively (**Figure 2**). Therefore, the electric energy consumption of Ti-Ru electrode is the least among these electrodes. The electric energy consumption of Ti-PbO_2 electrode is a little more than that of black lead electrode.

The electrodialytic cell then ran for 12 hours while other above conditions were kept. The variation of production concentration and current efficiency of product compartment with run time is shown in **Figure 3** and **Figure 4**.

As shown in **Figure 3** and **Figure 4**, after running for 12 hours, the product concentration for Ti-Ru, Ti-PbO_2, and black lead are 97.58 g/L, 93.76 g/L and 81.95 g/L, respectively. The current efficiency of product compartment for Ti-Ru, Ti-PbO_2, and black lead are 49.54%, 47.95% and 41.59%, respectively. In comparing the product concentration and current efficiency of product compartment, it is easy to deduce that the performance of Ti-PbO_2 anode is better than black lead anode and close to Ti-Ru anode.

Using electrodialytic cell applying Ti-PbO_2 as anode and running for 12 hours, the hypophosphorous acid was enriched. The density and concentration of the enriched hypophosphorous acid are 1.26 g/mL and 56.8％ respectively. The values of various targets in the enriched hypophosphorous acid are shown in **Table 1**. The product (enriched hypophosphorous acid) accords with the demand of analytical reagent.

Table 1 The values of various targets in the enriched hypophosphorous acid

Item	Value (％)
Cl^-	0.004
SO_4^{2-}	0.05
H_3PO_3	0.689
NaH_2PO_2	0.55
Heavy metal（Pb）	0.0008

As discussed above, within various aspects, Ti-PbO_2 electrode is an optimal anode and should be fitful for extensive industrial application in china.

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Received 20 October, 2003