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Abstract

Full Text

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Cathodic Deposition of Carbon from Molten Carbonates

Electrolysis of molten electrolytes (alkalis and chlorides) containing some amount of carbonates was at one time recommended for the production of alkali metals ([1-3]). Recently, researchers' interest in molten carbonates has again increased ([4]). In connection with this, we decided to study in greater detail their behavior during electrolysis.

For this purpose we investigated the electrolysis of an equimolar mixture of lithium and potassium carbonates using platinum and gold electrodes. The experiments were carried out in an open corundum cell with an isolated anodic space at a voltage of 2.5-4.5 V and at a temperature of 580-600°. The amount of electricity passed was determined by means of a copper coulometer. After electrolysis, the cathodic and anodic electrolysis products were analyzed.

It was established that the sole cathodic product is carbon in the form of a dense powdery deposit. The current yield of carbon at different voltages varied, within the limits of experimental error, around 100%. The anodic products are carbon dioxide and oxygen. Their ratio changes with increasing voltage in favor of carbon dioxide, but never exceeds the ratio $CO_2 : O_2 = 2 : 1$.

The source of carbon deposition at the cathode can only be the discharge of carbonate ions by one mechanism or another, for example

$$CO_3'' + 4e = C + 3O''. \tag{1}$$

The formation of carbon dioxide at the anode also presupposes the discharge of carbonate ions (directly or through dissociation):

$$2CO_3'' - 4e = 2CO_2 + 2O'' - 4e = 2CO_2 + O_2. \tag{2}$$

The oxygen content we found in the anodic gas exceeds the amount of it formed according to reaction (2). This fact requires the adoption of one of two assumptions: either not all the carbon dioxide formed according to reaction (2) enters the anodic space, or not only reaction (2) proceeds at the anode.

Fig. 1. Distribution of the amount of electricity (q_1/q_2) between reactions (4) and (5) and the ratio (n) of anodic gases

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The first assumption is possible for the case in which the discharge of the carbonate ion proceeds through its dissociation ([5]). Carbon dioxide evolution may then occur over the entire surface of the melt, while oxygen evolution occurs only in the anodic space as a result of the discharge of oxygen ions diffusing to the anode. This assumption was tested by carrying out control experiments in which the gas collected from the entire electrolyzer was analyzed. The ratio of carbon dioxide to oxygen in this gas was always less than two.

Thus, the additional amount of oxygen liberated at the anode is due to the occurrence of a parallel process of discharge of oxygen ions. Since the sole cathodic process is reaction (1), the source of the additional oxygen can only be

oxygen ions formed by this reaction. Consequently, at the anode, in addition to reaction (2), there also occurs discharge of the oxygen ions formed at the cathode:

$$2O'' - 4e = O_2. \tag{3}$$

Summation of reactions (1) and (2), and of reactions (1) and (3), gives two overall parallel processes taking place in the electrolyzer:

$$3CO_3'' = C + 2CO_3 + O_2 + 3O'', \tag{4}$$

$$CO_3'' = C + O_2 + O''. \tag{5}$$

The above considerations make it possible to calculate the total anodic current efficiency. For both reaction (4) and reaction (5), four electrons are required. Therefore, the total efficiency is calculated from oxygen, without taking into account the carbon dioxide evolved. At all voltages investigated by us it fluctuated around 100%.

Figure 1 gives the ratios $CO_2 : O_2 = n$ and the ratios between the first and second processes (by amount of electricity), calculated from these ratios according to reactions (4) and (5).

The polarization curves of the cathodic and anodic processes, obtained on a low-frequency polaroscopic installation ([6]) with the aid of platinum electrodes, show one wave each, which corresponds to two processes at the cathode and two processes at the anode.

Fig. 1. Distribution of the amount of electricity (q_1/q_2) between reactions (4) and (5) and the ratio (n) of anodic gases

On the basis of the data obtained, it does not appear possible to draw conclusions about the mechanism and stages of the cathodic process. The limiting current of the anodic process is governed by the rate of diffusion of oxygen ions, formed by reaction (1), from the cathode to the anode and, to some extent, by the rate of their diffusion from the bulk of the melt ([5]) after thermal dissociation of the carbonate. This also explains the fact that, with increasing current density, the ratio $CO_2 : O_2$ approaches two.

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Note: Figure translations are in progress. See original paper for figures.