საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 11, №3, 2017
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 11, no. 3, 2017

Physical Chemistry

Preparation of Manganese Dioxide in the Bipolar Electrolyzer

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ABSTRACT. **Manganese containing ores are among the main resources of Georgia. Electrolytic manganese dioxide (EMD) is a valuable product of its electrochemical processing. EMD is cathode material for the most abundant chemical current source (CCS) all over the world. Presented work is dedicated to two existing tendencies in the electrochemical technology: replacement of costly metallic electrode materials by new inexpensive carbon ones and substitution of monopolar electrolyzers by bipolar ones. In the paper the electrochemical characteristics of preparation of EMD are determined and compared in the case of monopolar and bipolar connection of the electrodes. Efficiency of the mentioned changes as well as of the use of carbon fiber material is shown. The reasons of this efficiency are explained.** *© 2017 Bull. Georg. Natl. Acad. Sci.*

Key words: electrolysis, monopolar and bipolar electrolyzer, manganese dioxide, current chemical source, carbon-fiber material.

Manganese dioxide is a cathode material for the most abundant (about 90% of retail production) chemical current source (CCS) of MnO_2-Zn system all over the world [1]. The large-tonnage manufacture of the most active modification – electrolytic manganese dioxide (EMD) operated in Rustavi Chemical Factory in the last quarter of the past century (the one in the former USSR) [2]. Demand of domestic, industrial, transport, scientific and military fields for the mentioned CCS is constantly increasing. This fact is due to the following advantages: wide range of electric capacity and power, great choice of size and shape, cheapness and service simplicity. Moreover, collection and utilization of the used CCS is not organized in the most countries world-wide, including Georgia. As a result, many harmful compounds, used in CCS penetrate into the nature. Therefore, reduction in price of the electrosynthesis of EMD and improvement of the characteristics of CCS of corresponding system (for example, increase of the degree of the use of the compounds) is the technical and economic as well as the environmental problem. It should be noted that

Table 1. Electrosynthesis of EMD at titanium anodes

N	Process characteristics	Dimensions	Monopolar connection	Bipolar connection
1	Current force	A	6.6	1.1
2	Anode current density	mA/cm^2	10	10
3	Cathode current density	mA/cm^2	5	5
4	Current volume density	A/l	0.65	0.65
5	Voltage on electrolyzers	V	2.72	13.74
6	Current efficiency	%	105.5	105.9
7	Power specific consumption	kW•h/kg	1.530	1.344

the electrochemical processing of Chiatura manganese ores is the important resource for development of Georgian economics.

Presented work is dedicated to the two existing tendencies in the electrochemical technology: replacement of costly metallic electrode materials by inexpensive carbon ones and substitution of monopolar electrolyzer by bipolar one. The efficient use of carbon (pyrolytic, polymeric, fiber, colloidal, composite and etc.) materials in the electrochemistry is determined by such properties as a highly developed surface, good electric conductivity, stability in aggressive medium, reasonable mechanical strength and heat-resistance. For example, carbon-fiber materials (CFM) are manufactured in the form of filament, bundle, rope, cloth and felt which offer strong possibilities for the selection of electrode structure [3]. It should be also noted about the possibility of the modification of the properties of mentioned materials by electrochemical method [4]. As to the bipolar electrolyzers – they are characterized by larger compactness, lesser consumption of construction materials and electric power and by service simplicity than monopolar electrolyzers [5].

Research Procedure. The electrolysis was carried out in the optimal conditions for preparation of manganese dioxide and hydrogen [2]: concentration of $MnSO_4$ – 100-120 g/l; concentration of H_2SO_4 – 15 -25 g/l; anode and cathode current densities – 9-12 mA/cm^2 and 5-10 mA/cm^2, respectively; solution temperature – 90-94^{0}C; electrolyzer – volume 2l; amount of electrolyzers – 5-6. Sulfuric acid, separated in the process, was neutralized by electrolytic manganese. The main characteristics of the electrosynthesis are current efficiency and specific power consumption.

For estimation of the quality of the obtained anode product a procedure, elaborated for determination of electrochemical activity of MnO_2 in the model current source of MnO_2/KOH/Zn/ system was used. Discharge of galvanic cells was carried out at the resistance of 20 Ohm in constant regime up to the final voltage, 0.9V, at room temperature. Discharge electric capacity is a main characteristic of the process.

The yield of cathode product of considered process – hydrogen is not used in EMD production because of its low economic efficiency (in comparison with the anode product) [2]. Therefore, in present work the main attention is focused on the anode process – preparation of EMD and on its quality.

Experimental Results and Discussion. In the multi-stage production of EMD the most important and, problematic is the process of electrosynthesis and especially anode processing. Worldwide only titanium is used as the anode material [6]. Therefore, the first part of the paper involves comparison of the characteristics of the monopolar and bipolar electrolyzers by the use of titanium anodes and graphite cathode (Table 1).

At monopolar operation of the electrodes the current – 6.6A was feeding to parallel connected 6 electrolyzers and 1.1A – to serially connected 6 electrolyzers at bipolar operation of the electrodes, that is to say, at the same value (6.6A) of the efficient current. As evident from Table 1, power specific consumption in bipolar electrolyzers is less by 12 %.

Further experiment involves the comparison of EMD electrosynthesis in monopolar and bipolar bathes at the use of the bundle of carbon fiber mate-

Table 2. Electrosynthesis of EMD at the anodes of carbon fiber material

N	Process characteristics	Dimensions	Monopolar connection	Bipolar connection
1	Current force	A	2.8	0.56
2	Anode current density	mA/cm	5.7-20.0	5.7-20.0
3	Cathode current density	mA/cm^2	2.54(average)	2.54
4	Current volume density	A/l	0.33(average)	0.33
5	Voltage on electrolyzers	V	2.94	14.13
6	Current efficiency	%	109.0	109.5
7	Power specific consumption	kW•h/kg	1.634	1.513

rial as the anodes. In this case the anode current density in the electrolyzers varied from 5.7 mA/cm^2 to 20 mA/cm^2. In Table 2 the electrotechnical characteristics of these processes are presented for 5 electrolyzers.

As evident from Table 2, power specific consumption in bipolar electrolyzer is less by 7.4 % in comparison with monopolar one. In both experiments the current efficiency is unchanged practically at the variation of the mode of electrode connection (Tables 1 and 2). This fact clearly demonstrates that this important characteristic of electrochemical process primarily depends on electrode material, all factors being the same.

The necessary condition for transition from monopolar mode of electrodes connection to bipolar mode was the identity of the characteristics of the electrochemical process (current density, solution concentration and temperature, electrodes sizes and the distances between them). Special attention was focused on precise repetition of the state of the surface of the reaction area of the electrodes. To avoid so called current drain all electrochemical cells were placed in separated glasses.

Consideration of the data of presented Tables involves two conventions: 1. Current efficiency is calculated by the amount of EMD – the product deposited at the anode which contains a reasonable quantity of crystallization water in addition to $MnO_{2,}$ low oxides of manganese and other impurities. Respectively, current efficiency exceeds 100%; 2. Because of the difficulties of calculation of real surface of CFM bundle anode, current density is given in the units - mA/cm.

In our opinion, reduction of power specific consumption in the bipolar electrolyzers in the course of the experiment is mainly caused by reduction of the voltage drop and by reduction of Joule heat outside of the electric network (between the rectifier of alternating current and the series of the electrolyzers). In this section the current force decreases from 6.6A to 1.1A in the first case (Table 1) and from 2.8A to 0.56A in the second one (Table 2). It is well-known that the voltage drop is proportional to the current force and the heat effect is proportional to its square.

After milling of EMD, deposited on CFM together with the electrode and after corresponding chemical treatment it was used as the cathode material for alkaline CCS. Table 3 shows the main characteristics of the galvanic cells manufactured on the basis of the products obtained on CFM and titanium anodes.

As evident from Table 3, the electrochemical activity of EMD, prepared on CFM, exceeds the corresponding value for the product obtained on titanium. This fact confirms our results[7], according to which the impurity of CFM in the cathode material of CCS improves its electrotechnical properties.

Bipolar electrodes, used in both above described experiments, involved two materials: titanium and graphite in the first case and CFM and graphite in the other one. Further experiment was performed by the use of a single material – low-ash electrode graphite (LEG). One side of each electrode, placed in the electrolyzer of the box shape, was operated as the anode and other side - as the cathode. As in the previous cases, for demonstration of the efficiency of bipolar electrolyzer, LEG electrodes also operated as monopolar one. In Table 4 the electrotechnical

Table 3. Electrochemical characteristics of CCS

N	Electrochemical characteristics	Dimension	Titanium anode	CFM anode
1	Open network voltage	V	1.49	1.49
2	Initial voltage	V	1.35	1.39
3	Mean voltage of discharge	V	1.02	1.09
4	Specific electric capacity	mA•h/g	157.2	166.2

Table 4. Electrosynthesis of EMD on LEG electrodes

N	Process characteristics	Dimensions	Monopolar ectrolyzer	Bipolar electrolyzer
1	Solution volume	l	2.5	2.5
2	Amount of electrodes		4	4
3	Current load of electrolyzer	A	0.75	0.25
4	Current force in electrochemical cell	A	0.25	0.25
5	Current efficiency	%	96.2	99.1
6	Specific power consumption	kW•h/kg	2.171	2.015

characteristics of these two processes are presented.

As evident from Table 4, in bipolar electrolyzer the current efficiency is more by 3% and specific power consumption is less by 7.2% than in monopolar one. The reasons of this fact, apart from above - mentioned, are the following: a) small potential drop in electrode depth in comparison to the same value in electrode length; b) exclusion of contact potential drop on intermediate electrodes. It should be noted that in the case of the use of isolated electrochemical bathes (Tables 1, 2) current efficiency exceeds this value for integrated bath (Table 4). This fact is determined by current leakage, characteristic of the latter [5]. The total elimination of this disadvantage is impossible and its reduction for specific process requires a concrete engineering decision. As to the fact that current efficiency in bipolar electrolyzer exceeds the similar value in monopolar one (Table 4), in our opinion, this fact is caused by such positive property of integrated bipolar electrolytic bath that the current is uniformly distributed on the whole working surface of the electrode [5].

Conclusions

Power specific consumption decreases by 9% on average, passing from electrode monopolar connection to bipolar one in the course of the electrosynthesis of MnO_2.

Electrolysis current efficiency at CFM anodes is 3-4% higher in comparison to titanium anodes.

Decrease of power consumption at passing from monopolar electrolyzer to bipolar one is caused by the losses of heat energy and voltage in outer as well as in inner sections of electric network of monopolar electrolyzer.

Acknowledgement. The work is fulfilled with financial support of Shota Rustaveli National Science Foundation (Grant #FR/208/3-200/14).

ფიზიკური ქიმია

მანგანუმის დიოქსიდის მიღება ბიპოლარულ ელექტროლიზერში

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მანგანუმის შემცველი მადნები საქართველოს ერთ-ერთი ძირითადი სიმდიდრეა. მათი ელექტროქიმიური გადამუშავების მნიშვნელოვანი პროდუქტია მანგანუმის ელექტროლიზური დიოქსიდი (მედ). იგი მსოფლიოში ყველაზე გავრცელებული დენის ქიმიური წყაროს (დქწ) აქტიური საკათოდე მასალაა. წარმოდგენილი სამუშაო ესადაგება ელექტროქიმიურ ტექნოლოგიაში დღეს არსებულ ორ ტენდენციას: ძვირადღირებული ლითონური საელექტროდე მასალების ჩანაცვლება ახალი თაობის იაფი ნახშირბადული მასალებით და მონოპოლარული ელექტროლიზერების შეცვლა ბიპოლარულით. სტატიაში განსაზღვრული და შედარებულია მედ-ისა და წყალბადის მიღების ელექტროტექნიკური მახასიათებლები ელექტროდების მონოპოლარული და ბიპოლარული ჩართვის შემთხვევებში. ნაჩვენებია აღნიშნული ცვლილებებისა და ნახშირბადულ-ბოჭკოვანი მასალის გამოყენების ეფექტურობა. ახსნილია ამ ეფექტურობის მიზეზები.

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Received June, 2017