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# Experimental Study of Electrolytic Metallic Manganese and Electrolytic Manganese Dioxide Simultaneous Electrosynthesis in MA-40 Anion-Exchange Membrane Reactor

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**ABSTRACT.** The process of simultaneous production of electrolytic manganese metal (EMM) and electrolytic manganese dioxide (EMD) has been studied using a lab-scale plate-parallel electrochemical reactor divided by MA-40 anion-exchange membrane. Separate circulation of the anolyte with  $32\text{--}47\text{ gL}^{-1}\text{ Mn}^{2+}$ ,  $20\text{ gL}^{-1}\text{ H}_2\text{SO}_4$ , treated at  $94^\circ\text{C}$  temperature and  $350\text{ Am}^{-2}$  current density and of the catholyte with  $25\text{--}30\text{ gL}^{-1}\text{ Mn}^{2+}$ ,  $150\text{--}160\text{ gL}^{-1}\text{ (NH}_4)_2\text{SO}_4$  at  $25\text{--}30^\circ\text{C}$ ,  $\text{pH} = 7.2\text{--}7.5$  and  $100\text{ Am}^{-2}$  current density was maintained.  $75\text{--}80\%$  current efficiency of EMM with  $99.9\%$   $\alpha\text{-Mn}$  has been achieved at the cathode, while EMD with  $91.5\%$   $\gamma\text{-MnO}_2$  was deposited at the anode with  $98.8\%$  current efficiency. © 2008 Bull. Georg. Natl. Acad. Sci.

**Key words:** EMD,  $\text{MnO}_2$  electrosynthesis, EMM, manganese metal electro-deposition, electrochemical reactor, anion-exchange membrane.

Georgia is rich in deposits of manganese ores and on-site electrochemical processing with manufacturing of most valuable manganese products is an important goal of domestic economy. Same compound - manganese sulphate was used as an electrolyte and similar industrial flow sheets of hydrometallurgical processing of manganese ores were implemented since the early 1940s in large-scale industrial plants which operated in this country separately for electrolytic manganese metal (EMM) and for electrolytic manganese dioxide (EMD) production as numerous efforts /1-3/ of simultaneous production of these products not only in one electrolytic cell, but even in the joint hydrometallurgical circle have not been successful to the present day. The conventional cell for EMM production is divided by flowing through cotton or PCHV diaphragm, which cannot prevent penetration of ammonia-ions, presented as a buffer to sustain the neutral pH conditions in the catholyte in high

( $160\text{--}180\text{ gL}^{-1}$ ) concentrations [4], while  $\text{NH}_4^+$ -ion is absolutely undesirable in EMD production, for it lowers its activity in batteries [5, 6]. Difference in electrolyte temperatures ( $<35^\circ\text{C}$  for EMM and  $>90^\circ\text{C}$  for the EMD production) is another problem as well as the possibility of waste hydrogen evolution at the cathode during  $\text{MnO}_2$  generation at the anode of the undivided cell, and waste oxygen evolution occurs at the anode during the manganese electro-deposition at the cathodes in the existing EMM plants equipped with flowing through diaphragms. Penetration of the acidic anolyte with suspended  $\text{MnO}_2$  particles into the cathodic area through the diaphragm is also a problem, causing the corrosion of manganese metal deposited at the cathode. So the energy consumption, investment and running costs are doubled, as two plants are constructed instead of one.

Utilization of highly selective anionic membranes (AEM) able to prevent penetration of non-desirable am-

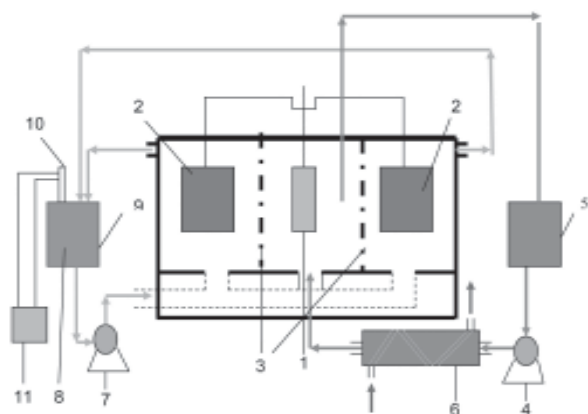
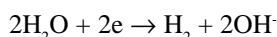


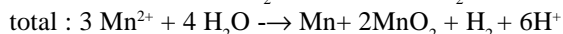
Fig. Laboratory plant for simultaneous production of EMM and EMD

monia-ions into the anolyte created the basis for the novel process of simultaneous production of these products in one cell [7-9]. Manganese is a most electro-negative metal which can be deposited from aqueous solutions, so electrolysis of water proceeds simultaneously with electro-deposition of EMM and EMD:

at the cathode:  $\text{Mn}^{2+} + 2e \rightarrow \text{Mn}$



at the anode:  $2\text{Mn}^{2+} + 4\text{H}_2\text{O} - 4e \rightarrow 2\text{MnO}_2 + 8\text{H}^+$



Some experimental data obtained in the investigation of the joint process using the plate-parallel cell divided by MA-40 anion-exchange membrane (AEM) in conditions when the known optimal solution temperatures were maintained using the external heat-exchangers for each of the independently circulated electrolytes ( $>90^\circ\text{C}$  in the anolyte for EMD electro-synthesis and  $<35^\circ\text{C}$  in the catholyte for EMM electro-deposition) are presented below.

Electrolyte solutions were prepared using distilled water and chemically pure  $\text{MnSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  reagents. The impurities were removed from the electrolyte by standard procedures of precipitation in hydroxide

(ferrous and ferric ions), sulfide (Ni and Co ions by treating with  $(\text{NH}_4)_2\text{S}$  and  $\text{Al}_2\text{S}_3$  addition) and adsorption (at  $\text{MnO}_2$  and activated carbon) forms. The content of  $\text{MnO}_2$  was determined by the standard oxalate method, while  $\text{Mn}^{2+}$ -ions were analyzed by potentiometric titration and Volhard methods and  $\text{NH}_4^+$ -ions- by ammonia distillation method. The pH-673 type device was used for pH measurements. The structures of metallic manganese and manganese dioxide were determined by X-ray pattern analysis at diffraction – DRON -3M device. A VT1-0 type plate titanium sheet was used as anode material, while a stainless steel plate was used as a cathode.

The principal scheme of the laboratory loop for simultaneous production of EMM and EMD is presented in the (Fig.). The cathode (1), placed in the central department of the acrylic cell, was divided from two anodes (2), placed in outer departments by MA-40 type anion-exchange membranes (3). 1 liter of catholyte was circulated by means of centrifugal pump (4) through the intermediate vessel (5) and water cooler (6) which ensures cooling of the solution from  $25\text{-}30^\circ\text{C}$  at the outlet of the cell to  $14\text{-}15^\circ\text{C}$  at the inlet. Another pump (7) is used for the circulation of 2 liters of anolyte through the intermediate vessel (8) equipped with heater (9), contact thermometer (10) and regulation system (11), able to maintain up to  $95^\circ\text{C}$  in the anode department.

Due to quantitative chemical analysis  $\text{NH}_4^+$ -ions were not identified in the anolyte. The results of simultaneous production of EMM and EMD are shown in (Table). As is seen from these data, both of the products are produced by high current efficiency (71.4 – 80% for EMM and 96.5 – 98.8% for EMD). Due to chemical and X-ray pattern analysis of electro-deposited samples  $\tilde{a}$  – manganese with chemical composition (%): Mn – 99.9, Fe – 0.009, Ni – 0.019, S – 0.018, C – 0.002, P – 0.001 has been deposited at the anode, while the compact EMD containing (%):  $\tilde{a}$  –  $\text{MnO}_2$  – 91.52,  $\text{SO}_4^{2-}$  – 0.87, Ti – 0.039,  $\text{H}_2\text{O}$  – 2.86 was obtained at the anode.

Table

EMM and EMD simultaneous production in ion-selective membrane electrolyzer  
 Experimental conditions: current – 0.5 A, cathode current density -  $350\text{ Am}^{-2}$ , anode current density -  $100\text{ Am}^{-2}$ ,  
 volume current density: in catholyte –  $0.5\text{ AL}^{-1}$ , in anolyte –  $0.25\text{ AL}^{-1}$ , voltage – 4.8 V.

Ah	t, °C		pH catholyte		Mn <sup>2+</sup> , gL <sup>-1</sup>				(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , gL <sup>-1</sup>		η Mn, %	η MnO <sub>2</sub> , %	MnO <sub>2</sub> , % in the product	Specific energy consumption, kW-h kg <sup>-1</sup>
					catholyte		anolyte		catholyte					
	catholyte	anolyte	init	fin.	init	fin	init.	fin	init.	fin .	fin			
0.94	94	25	6.5	6.1	35.0	34.2	32.2	31.2	146.0	145.87	71.4	96.52	90.68	1.95
1.04	93	27	7.6	5.5	34.35	33.4	33.7	32.6	146.0	145.74	80.0	97.6	91.35	1.84
1.12	94	27	7.5	7.3	34.16	33.2	37.2	35.9	151.4	151.23	76.5	98.8	91.50	1.86
2.42	94	27	7.2	7.3	33.5	31.4	47.2	44.9	143.0	142.79	73.4	98.3	91.43	1.88

ქიმიური ტექნოლოგია

## ელექტროლიზური ლითონური მანგანუმისა და ელექტროლიზური მანგანუმის დიოქსიდის ერთდროული ელექტროსინთეზის ექსპერიმენტული შესწავლა MA-40 მემბრანულ რეაქტორში

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(წარმოდგენილია აკადემიკოს გ. ცინცაძის მიერ)

წარმოდგენილ ნაშრომში ნაჩვენებია, რომ ელექტროლიზერში, რომელშიც სადიაფრაგმო მასალად გამოყენებულია ანიონტური მემბრანა MA-40, ერთდროული პროცესის შედეგად მიღებულია მაღალი სისუფთავის ელექტროლიზური ლითონური მანგანუმი (99,9%) და აქტიური ელექტროლიზური მანგანუმის დიოქსიდი, მასში პროდუქტის შემცველობით (91,5%), დენითი გამოსავლებით (80%, 98,8%),

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