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Scientific paper
UDC:621.793.1=20

Electrochemical Properties of Commercially Available $M_{(n+1)}AX_n$ Phases in the Process of HCl Electrolysis

Electrochemical properties of commercially available $M_{(n+1)}AX_n$ phases (Ti_3SiC_2 and Ti_2AlC), as a cathode and anode materials in the process of the electrolysis of HCl are investigated. It is shown that Ti_3SiC_2 passivates at anodic potentials, being promising substrate for application of catalytic coating for chlorine evolution (mixture of TiO_2 and RuO_2). At the same time it is found that overvoltage for the hydrogen evolution onto Ti_3SiC_2 as cathode is for 0.5 V lower than that on commercially used graphite electrodes. By using activated anodes and Ti_3SiC_2 as cathodes instead of graphite ones, the voltage saving on the industrial cell for chlorine production by the electrolysis of HCl would amount to about 0.67V.

1. INTRODUCTION

As a consequence of the significant increases in energy costs and the increased scarcity of industrial fuel supplies, intensive research in the field of electrolysis has been performed in order to reduce the amount of power used in industrial electrolysis processes. The cost of electrolysis is proportional to the voltage at which the electrolysis is performed. Thus, it is desirable to reduce the amount of voltage at which a solution is electrolyzed to as low of a value as possible.

The introduction of "dimensionally stable anodes" (DSA) into the processes of chlorine, chlorate and hypochlorite production by the electrolysis of brine has led to significant decreases in energy costs [1]. DSA are made of titanium coated with a thermally prepared mixture of TiO_2 and RuO_2 . DSA are corrosion resistant, selective to chloride ion oxidation and exhibit a high catalytic activity. However, the coating must be routinely replaced.

In certain industrial operations hydrochloric acid is formed as a by-product of chlorination (production of TDI etc.). There is usually no immediate market for the hydrochloric acid. The lack of a market makes hydrochloric acid production problematic in that it cannot be dumped

into sewers and wastewater outlets without costly neutralization. It has been customary in industry to utilize electrolysis of hydrochloric acid to overcome disposal issues. A number of commercial processes of electrolysis of hydrochloric acid for production of chlorine have been developed [2]. A currently employed commercial electrochemical process is known as the Uhde process [3]. In this process aqueous HCl solution of approximately 22 wt. % is fed at 65 °C to 70 °C into an electrochemical cell into both the anodic and cathodic compartments which are divided by a diaphragm made of special type of PVC cloth. Graphite is used as electrode material for both, anode and cathode (bipolar electrode). Exposure to a direct current in the cell results in an electrochemical reaction and a decrease in HCl concentration of up to 17 wt. % with the production of chlorine gas in the anodic compartment and hydrogen in the cathodic compartment. Both the anode and cathode side of a graphite bipolar electrode, undergo severe destruction after operating for some time in a cell for hydrochloric acid electrolysis [3]. The use of DSA in this process is not recommended since the titanium substrate undergoes significant corrosion in concentrated HCl at high temperatures and the electrode becomes unusable after a short operating time. Other materials stable in hydrochloric acid like platinum group metals are excessively expensive.

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In this paper an attempt was made to replace graphite as electrode material for HCl electrolysis with commercially available $M_{(n+1)}AX_n$ phases and results of the investigation of hydrogen and chlorine evolution on these materials are shown and compared with the commercially used graphite electrodes.

2. WHAT ARE $M_{(N+1)}AX_N$ Phases

$M_{(n+1)}AX_n$ phases are known as new class of solids, thermodynamically stable nanolaminates (detailed review given in Ref. [4]), where M is an early transition metal, A is an A-group element (mostly IIIA and IVA groups of the periodic system of elements) and X is either C and/or N, with n varying from 1 to 4. All $M_{(n+1)}AX_n$ phases discovered so far are presented in Table 1. Typical characteristic of all $M_{(n+1)}AX_n$ phases is that they are stable in a very narrow range of composition (2-3 at. %) in the phase diagrams [5]. It is also

characteristic for $M_{(n+1)}AX_n$ phases that are layered hexagonal (space group $D_{6h}^{4} - P6_3/mmc$) with two formula per unit cell. Figs. 1a, b and c compare the unit cells of the 211, 312 and 413 phases [4]. In each case near close-packed layers of M layers are interleaved with layers of pure group A-element, with the X-atoms filling the octahedral sites between the former. The A-group elements are located at the center of trigonal prisms that are larger than the octahedral sites and thus better able to accommodate the larger A-atoms. The M_6X octahedra are edge sharing and are identical to those found in the rock salt structure of the corresponding binary carbides [4]. The main difference between the structures shown in Fig. 1 is the number of M layers separating the A-layers: in the 211's there are two; in the 312's, three and in the 413's four. This layering is crucial and fundamental to understanding the properties in general, and the mechanical properties in particular.

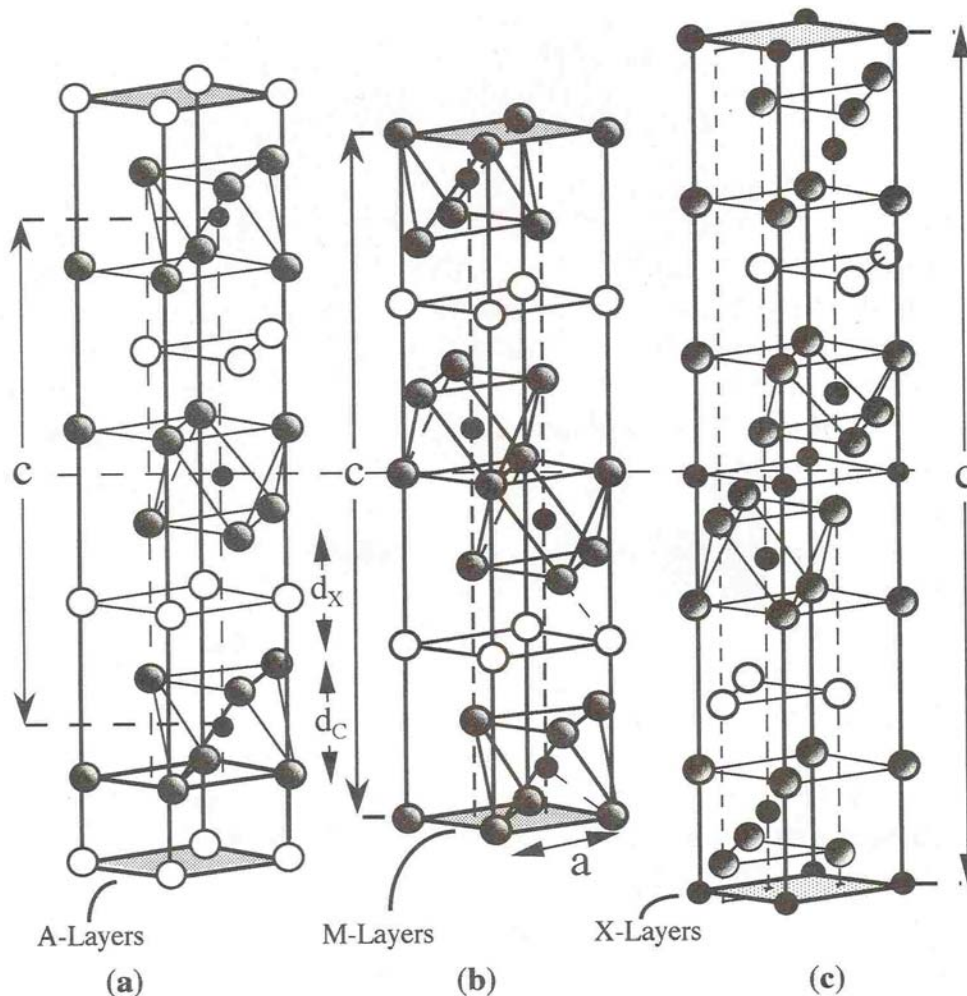


Fig. 1. Unit cells of, (a) 211, (b) 312 and (c) 413 phases. Unit cells are delineated by vertical arrows labeled c. The horizontal dashed line is drawn through the centers of the unit cells.

Table 1: Summary of $M_{(n+1)}AX_n$ phases known to date

IIB	IIIB	IVA	VA	VIA
	Al	Si	P	S
	Ti ₂ AlC	Ti ₃ SiC ₂	V ₂ PC	Ti ₂ SC
	V ₂ AlC		Nb ₂ PC	Zr ₂ SC
	Cr ₂ AlC			Nb ₂ SC _{0.4}
	Nb ₂ AlC			Hf ₂ SC
	Ta ₂ AlC			
	Ti ₂ AlN			
	Ti ₃ AlC ₂			
	Ti ₄ AlN ₃			
Zn	Ga	Ge	As	Se
	Ti ₂ GaC	Ti ₂ GeC	V ₂ AsC	
	V ₂ GaC	V ₂ GeC	Nb ₂ AsC	
	Cr ₂ GaC	Cr ₂ GeC		
	Nb ₂ GaC	Ti ₃ GeC ₂		
	Mo ₂ GaC			
	Ta ₂ GaC			
	Ti ₂ GaN			
	Cr ₂ GaN			
	V ₂ GaN			
Cd	In	Sn	Sb	Te
Ti ₂ CdC	Sc ₂ InC	Ti ₂ SnC		
	Ti ₂ InC	Zr ₂ SnC		
	Zr ₂ InC	Nb ₂ SnC		
	Nb ₂ InC	Hf ₂ SnC		
	Hf ₂ InC	Hf ₂ SnN		
	Ti ₂ InN			
	Zr ₂ InN			
	Tl	Pb	Bi	Po
	Ti ₂ TlC	Ti ₂ PbC		
	Zr ₂ TlC	Zr ₂ PbC		
	Hf ₂ TlC	Hf ₂ PbC		
	Zr ₂ TlN			

Until recently only structural, mechanical and electrical properties of $M_{(n+1)}AX_n$ phases were investigated [4], while electrochemical behavior of $M_{(n+1)}AX_n$ phases was first reported in 2003 [6]. After that, another three papers concerning electrochemical properties of $M_{(n+1)}AX_n$ phases [7-9] and one US patent [10] were published to date. It is shown that some $M_{(n+1)}AX_n$ phases passivate in acidic and alkaline media (Ti₃SiC₂, Ti₃GeC₂, Ti₂AlN, Ti₄AlN₃), while some of them undergo active dissolution (Ti₂AlC, V₂AlC, Cr₂AlC) [9]. Phases that passivate were considered as suitable for substrates that should be activated with the mixture of TiO₂ and RuO₂ (DSA) and used as anodes in the electrolysis of HCl [10]. At the same time, it is discovered that Ti₃SiC₂ is a promising cathode for the electrolysis of HCl [10]. Since nowadays only two $M_{(n+1)}AX_n$ phases are commercially available [11], and these are Ti₃SiC₂ and Ti₂AlC. These two materials were tested as electrodes for the electrolysis of HCl.

3. EXPERIMENTAL

All experiments were carried out in a three-compartment standard electrochemical cell at room temperature. The platinum foil counter electrode and the reference - saturated calomel electrode, SCE, were placed in separate compartments. The latter was connected to the working electrode by a Luggin capillary. Solution of HCl was made from analytical grade HCl and pure water (EASY pure UV, 18.3 MΩ, Barnstead).

Polarization measurements were performed by a computer-controlled potentiostat (PAR M273A) - using the corrosion (PAR M352/252, version 2.01) software, with the sweep rate of 1 mV s⁻¹. For obtaining polarization curves corrected for IR drop, current interrupt technique was used with time of current interruption being 0.5 s.

Samples (10x10x0.25 cm³) were sealed in an epoxy resin such that only 1 cm² was exposed to the solution. Once mounted they were polished down to 0.05 μm alumina impregnated polishing cloths, cleaned in an ultrasonic bath for 10 min., thoroughly washed with pure water and transferred to the electrochemical cell.

Sample of Ti₃SiC₂ activated with the mixture of TiO₂ and RuO₂ (DSA) was obtained by the sol-gel technique using following procedure: Ti₃SiC₂

plates, 1 cm² in size, were used as coating substrates. The plates were sand-blasted and degreased in saturated NaOH ethanol solution. Equimolar mixture of RuO₂ and TiO₂ sol, calculated to metal, was used to prepare oxide coating. Oxide sols were prepared separately by forced hydrolysis of RuCl₃ and TiCl₃ in boiling 0.27 M HCl water solution, under the reflux. The hydrolysis of RuCl₃ and TiCl₃ ran on for 46 and 10 h, respectively. Hydrolysis conditions were chosen according to the coating properties. Sol mixture, with solid phase concentration of 13.9 mg cm⁻³, was painted over the substrates in two layers, which give coating mass of 1.0 mg cm⁻², calculated to the overall oxide. Dispersing medium was evaporated at 70 °C, and then the gel phase of separate layers were annealed at 450 °C for 10 (first layer) and 30 min (second layer).

4. RESULTS AND DISCUSSION

In Fig. 2 are shown corrosion diagrams for Ti₃SiC₂ and Ti₂AlC in 22 wt. % HCl. As can be seen corrosion behavior of these two phases is different. Ti₃SiC₂ possess much more positive corrosion potential than Ti₂AlC (for about 0.65 V) and it passivates immediately after reaching corrosion potential, with the current density of passivation being about 1 mA cm⁻² and the passive region varying from about 0.5 V to 2.0 V (upper limit of potential – at more positive potentials chlorine evolution starts on this material). It is shown in previous papers [6-9] that the passive film formed at anodic potentials onto Ti₃SiC₂ is an n-type semiconductor, composed mainly of SiO₂ (with about 3 at. % of Ti) and that such passive film could be 10 μm thick after 4 days exposure to 1.4 V vs. Pt in 22 wt. % HCl [7]. Although corrosion behavior of Ti₂AlC is also characterized by the current plateau (between about -0.3 V and about 0.8 V), the value of current density for this plateau is about 40 mA cm⁻² and the current increases at more positive potentials. It is important to note that already in the region of a current plateau dissolution of Ti₂AlC occurs being accompanied by the change of solution color in the vicinity of the electrode surface from transparent to brown. Hence, it could be concluded that only Ti₃SiC₂ is stable in the investigated solution and that this material is a promising substrate for application of catalytic coating (mixture of TiO₂ and RuO₂) for chlorine evolution [6,10].

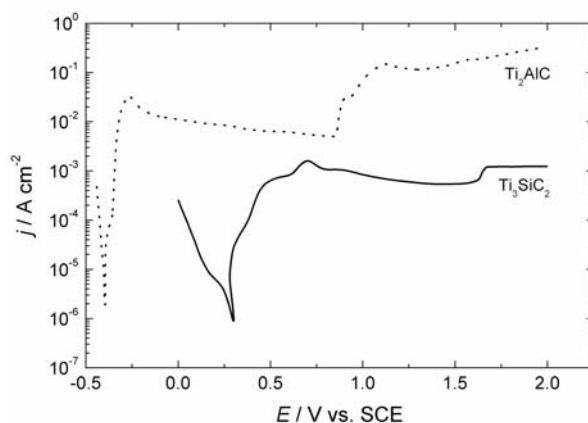


Fig. 2. Corrosion behavior of commercially available $M_{(n+1)}AX_n$ phases (Ti₃SiC₂ and Ti₂AlC) in 22 wt. % HCl at the room temperature.

These two materials are also tested for hydrogen evolution in the same solution. As can be seen in Fig. 3 the overvoltage for hydrogen evolution on Ti₃SiC₂ is for about 0.2 V lower than that on Ti₂AlC at the current density of 0.3 A cm⁻² (typical current density value for industrial chlorine production). It should be noted here that Ti₃SiC₂ is better catalyst for hydrogen evolution in HCl than all other $M_{(n+1)}AX_n$ phases investigated as cathodes in the process of HCl electrolysis (Ti₃GeC₂, Ti₂AlN, Ti₄AlN₃, V₂AlC, Cr₂AlC etc.).

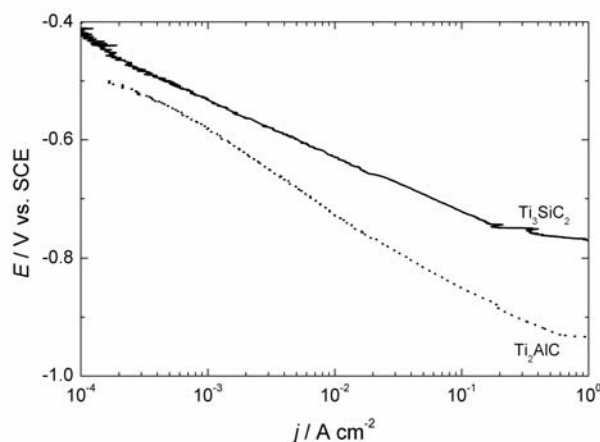


Fig. 3. Polarization diagrams for hydrogen evolution on commercially available $M_{(n+1)}AX_n$ phases (Ti₃SiC₂ and Ti₂AlC) in 22 wt. % HCl at the room temperature.

Hence, it was concluded that polarization characteristics of Ti₃SiC₂ and commercially used graphite (Kynar – impregnated graphite) should be compared in the process of hydrogen evolution

(cathodes), while these of Ti_3SiC_2 activated with a mixture of TiO_2 and RuO_2 and commercially used graphite should be compared for chlorine evolution (anodes). Such a comparison is presented in Fig. 4. As can be seen Ti_3SiC_2 and Ti_3SiC_2 activated with a mixture of TiO_2 and RuO_2 are much better cathodes and/or anodes than the commercially used graphite. Comparing the cell voltage at a current density of 0.3 A cm^{-2} it could be concluded that the voltage saving is about 0.67 V with the new type of cathodes and anodes.

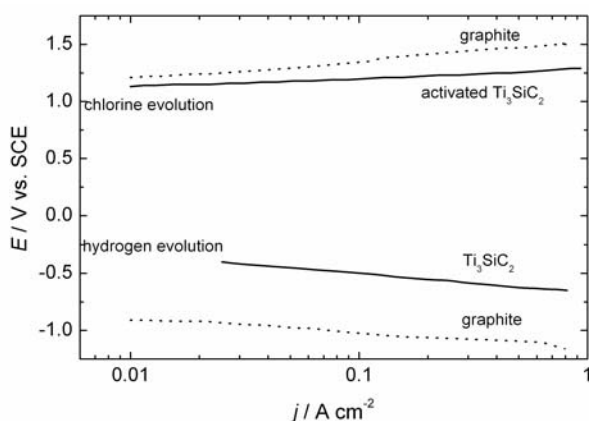


Fig. 4. Comparison of polarization diagrams for hydrogen and chlorine evolution on commercially used graphite electrodes and Ti_3SiC_2 (as cathode) and Ti_3SiC_2 activated with TiO_2 and RuO_2 mixture (as anode) in 22 wt. % HCl at the room temperature.

Chlorine is produced by currently employed commercial electrochemical process, known as Uhde process [3] in 14 plants placed in Germany, Belgium, France, Japan, USSR, Italy, China and USA with the total capacity of chlorine production of about 2000 tones per day. If we assume that only with application of our cathodes voltage on the cell would be reduced for 0.5 V (lower overvoltage for hydrogen evolution for 0.5 V), this would be saving in electric power for 25 %, taking into account that in industrial plants voltage on the cells is about 2.0 V . Hence for production of 2000 tones per day savings in energy consumption would amount to 800.000 kWh , or $2.92 \times 10^8 \text{ kWh}$ per year. Assuming that average price of electricity for industrial plants amounts to 5.22 Cents per kWh (data from USA in 2001.), this would amount to $\$15.242.400$ savings. Hence, it could be concluded that application of new electrode materials based on Ti_3SiC_2 would be very promising.

4. CONCLUSION

From the results presented in this paper it could be concluded that Ti_3SiC_2 could be successfully used as substrate for activation with TiO_2 and RuO_2 mixture and used as anode in the process of chlorine evolution by the electrolysis of HCl. At the same time Ti_3SiC_2 is much better cathode material than commercially used graphite for hydrogen evolution in the same process. Hence, significant savings in the cell voltage for this process could be made by application of these two materials in the industrial production of chlorine.

Acknowledgement

This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia under the innovative project "Development and testing of the prototype of the cell for chlorine production by the electrolysis of HCl", Project No. IP06-8038, 2006.

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REZIME**ELEKTROHEMIJSKE OSOBINE $M_{(N+1)}AX_N$ FAZA U PROCESU ELEKTROLIZE HCL**

U ovom radu ispitivane su elektrohemijske osobine komercijalno dostupnih $M_{(n+1)}AX_n$ faza (Ti_3SiC_2 i Ti_2AlC) kao katodnih odn. anodnih materijala u procesu elektrolize HCl. Pokazano je da se Ti_3SiC_2 pasivira na anodnim potencijalima i da predstavlja dobar materijal za nanošenje katalitičke prevlake na bazi smeše TiO_2 i RuO_2 (tzv. DSA). Takođe je pokazano da je prenapetost izdvajanja vodonika na Ti_3SiC_2 za 0.5 V manja od prenapetosti na komercijalnim elektrodama od grafita. Korišćenjem aktiviranih anoda i Ti_3SiC_2 kao katoda, umesto komercijalnih grafitnih anoda i katoda, ustanovljeno je da ušteda u naponu na industrijskoj ćeliji za elektrolizu HCl iznosi oko 0.67 V.