

## THE DEVELOPMENT OF SURFACE MODIFIED BIPOLAR GRAPHITE ELECTRODE FOR ELECTROWINNING OF ALKALI AND ALKALINE EARTH METALS

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Alkali and alkaline earth metals like sodium, magnesium etc. are produced most effectively by molten salt electrolysis. The bipolar technology is proved to be energy efficient and an easy method to increase the space-time yield of the electrolytic cells. Graphite plate cladded with a metal plate on one side of it is used as the bipolar electrode in electrowinning of magnesium. This is proved to be a costlier and not fully reliable one for longer operation of the cells. The life of such heterogeneous bipolar electrodes is normally short. A stable and long lasting bipolar electrode is the need of the hour. Non-stoichiometric transition metal carbides are good electronic conductors at high temperatures. These carbides are more stable and they are not get affected by the molten halides. Graphite plate having such carbide layer on one of its surface can replace the graphite-metal heterogeneous bipolar electrode for the electrolysis. The graphite surface was modified to titanium carbide by electrolytically depositing titanium metal on to the graphite surface from the titanium ion containing molten chloride system at around 1073 K. Formation of titanium carbide on the graphite surface was identified using XRD technique. The graphite rod with modified surface was used as cathode in electrolysing molten magnesium chloride. It was found that this graphite rod was stable while the plain graphite rod failed within an hour of electrolysis.

**Keywords:** Surface modification, Titanium carbide, Molten salt electroilsis.

### INTRODUCTION

Alkali and alkaline earth metals like sodium, magnesium etc. are produced most effectively by molten salt electrolysis [1,2]. The bipolar technology is proved to be energy efficient and an easy method to increase the space-time yield of the electrolytic cells [3,4]. Graphite plate cladded with a metal plate on one side of it (Fig. 1) is used as the bipolar electrode in electrowinning of magnesium[4]. Sputtering of metal over graphite surface, ion implantation, laser spraying of conducting ceramics like  $TiB_2$  etc. forming the surface film by pressing the powder on the graphite surface and sintering it, and cladding the surface with thick metal plate are the different techniques tried for the fabrication of a bipolar electrode. These were proved to be costlier and not fully reliable for longer operation of the cells. The life of such heterogeneous bipolar electrodes is normally short. A stable and long lasting bipolar electrode is the need of the hour.

Non-stoichiometric transition metal carbides are good electronic conductors at high temperatures (Table I) [5-7].

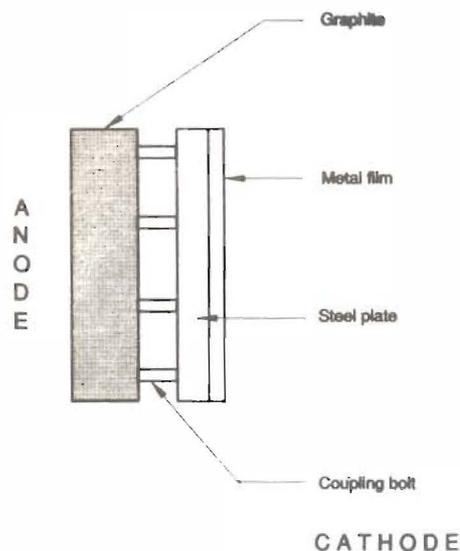


Fig. 1: Heterogeneous bipolar electrode

TABLE I: Physical properties of carbides

Carbides	Melting point K	Elect resist $\mu \Omega \text{ cm}$	Thermal exp $10^{-6} \text{ deg K}$
$\text{Li}_2\text{C}_3$	1073(d)		
$\text{MgC}_2$			
$\text{CaC}_2$	2573		
$\text{TiC}_{1-x}$	3530	200	8.31
$\text{ZrC}_{1-x}$	3803	182	6.95
$\text{Cr}_3\text{C}_2$	2168	75	117.00
SiC	3100(d)	$0.15 \times 10^6$	
Metals			
Carbon		50	5.70

These carbides are more stable [8] and they are not get affected by the molten halides. Graphite plate having such carbide layer on one of its surface can replace the graphite-metal heterogeneous bipolar electrode for the electrolysis. Chemical vapour deposition [9], electrochemical deposition [10], high temperature plasma spraying [11], mechanically pressing the carbide powder and sintering, and modifying the graphite surface by spraying metal on the graphite surface [12] or electrolytically depositing the metal on the graphite surface and then sintering to get metal carbide over the graphite surface are the possible ways to have the metal carbide layer on the graphite plate. Carbides of chromium and titanium top the list of electronic conductivity of transition metal carbides [13]. Hence titanium carbide is chosen for this study. Of all the above mentioned techniques electrodeposition of titanium metal on to the graphite surface from molten chloride melt containing titanium ions seems to be the simplest technique for having the titanium carbide layer on graphite surface.

The present study deals with the modification of the graphite surface to titanium carbide by this technique and characterising the modified layer.

### EXPERIMENTAL

Fig. 2 shows the cell assembly kept inside the vertical muffle furnace for conducting electrochemical studies. A graphite crucible kept in an iron jacket served as the container for holding the electrolyte and one of the electrode (anode) for conducting electrolytic studies. Provision for argon atmosphere also was incorporated in this setup. Graphite rod and 1.0 mm diameter molybdenum wire were used as working cathodes for conducting steady state voltametric studies. Molybdenum wire used in this study was

supplied/produced by Aldrich Chemicals Co, USA, and the graphite was obtained in the form of rods (HPC grade) and plates from Graphite India Ltd, Bangalore. AR grade potassium and sodium chlorides were dried under vacuum for about 6 hours prior to use in the study. Commercial pure titanium sheet was used in the form of strip for generating titanium ions in the chloride melt. Aplab 7252 model CVCC regulated DC power supply unit was employed as DC power source for conducting voltammetric studies as well as to conduct electrolysis studies.

Discharge potential of alkali metal ions in the 1:1 KCl-NaCl on molybdenum wire was determined to establish the reliability of the Ag/AgCl reference electrode used in this study. Discharge potential of alkali metal ions on the graphite surface with reference to the Ag/AgCl electrode was also determined.

The titanium ions were introduced into the 1:1 NaCl-KCl melt by anodically dissolving titanium strips. The current and the duration of dissolution were adjusted to have about 5 wt% of titanium dichloride in the chloride melt.

Cathodic discharge potential studies were carried out in the melt at different temperatures on molybdenum wire as well as on graphite rod. The minimum potential at which the titanium ion discharges on the graphite to form a compound was deduced from this study. The graphite rods were kept

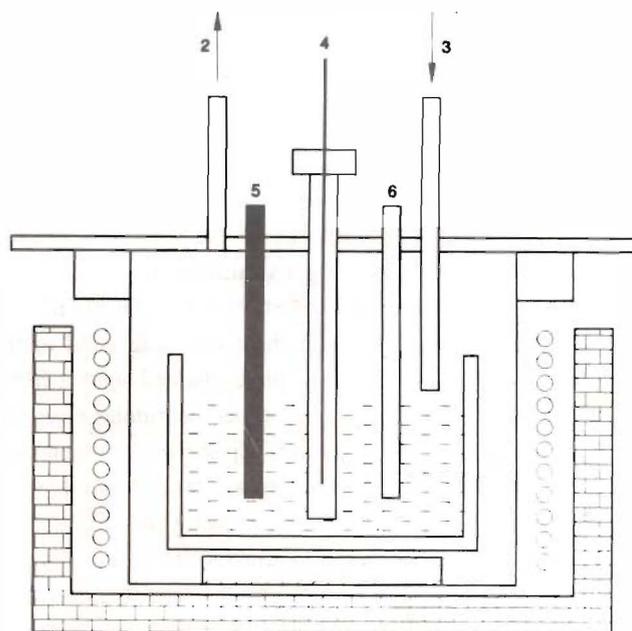


Fig. 2: Experimental cell

(1) Furnace (2&3) Argon in and out (4) Ag/AgCl ref  
(5) Graphite anode and (6) Cathode

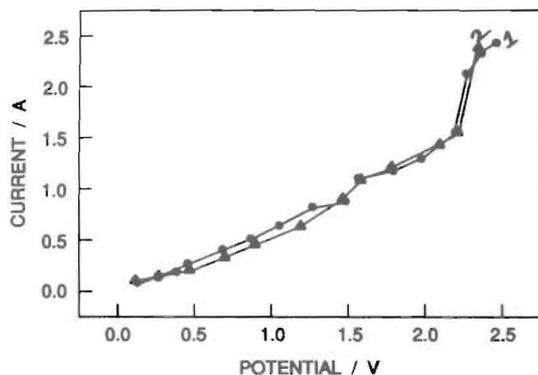


Fig. 3: Current voltage (Ag/AgCl) characteristics of molybdenum (1) and graphite (2) cathodes in 1:1 NaCl-KCl Melt containing titanium ions at 1083 K

in the electrolyte cathodically for different duration and at different temperatures. 10 x 10 mm square portion of the graphite rod was cut, cleaned, and analysed using AAS for the presence of titanium ions on its surface. XRD analysis of the graphite surface rods also performed to identify the formation of titanium carbide. The graphite surface was modified to titanium carbide by electrolytically depositing titanium metal on the graphite surface for different duration and at different temperatures. Stability of the modified graphite surface was tested by electrolysing the chloride melt containing about 15 wt% magnesium chloride. Electrolysing study was also carried out using plain graphite rod for comparing the performances.

### RESULTS AND DISCUSSION

The steady state potentiometric studies yielded a single value of discharge potential, 1.9 V for the alkali metals, viz., potassium and sodium present in the melt at equimolar ratio, on molybdenum at 1023 K. Kh.L. Strelets [14] reported 1.72 V for the same melt and explained that nearness of discharge potentials for potassium and sodium is the reason for obtaining the single discharge potential. The closeness of the discharge potentials obtained from this study and that reported in literature confirms the reliability of the Ag/AgCl reference electrode used in this study [15]. Fig. 3 shows the

TABLE II: Discharge potentials of titanium ions on molybdenum and graphite

Temp K	Discharge potential / V	
	Molybdenum	Graphite
813	1.2	0.6
1083	1.0	0.5

I-V characteristics of molybdenum and graphite cathodes in chloride melts containing about 5 wt% titanium dichloride. This figure shows that a sharp increase in current takes place for the molybdenum cathode near the potential corresponding to the discharge potential of titanium(II) ion to titanium metal; but the change is gradual for the graphite cathode. Table II presents the discharge potentials of titanium ion, derived from the I-V curves, on molybdenum and graphite cathodes at different temperatures. The discharge potential of titanium ion on graphite cathode is less than that on molybdenum cathode at all temperatures. The lower discharge potential of titanium ion on the graphite surface is attributed to its compound or alloy formation with carbon [16]. The possible compound is the titanium carbide, which is known to exist with varying stoichiometry. The scheme of reactions taking place at the graphite surface is presented in the Fig. 4. The formation of the titanium carbide is supported by the XRD studies on the modified graphite surface. The peaks observed on the samples are compared with the peaks for graphite, alpha titanium and stoichiometric titanium carbide. The peaks resemble more with titanium metal with the distorted lattice due to the presence of carbon at the interstitial positions rather than with titanium carbide. As the duration of the experiment is shorter and homogenisation of the layer was not attempted, the peaks do not coincide with the compound TiC [5].

Table III presents the stability of the modified graphite surface used for the electrolysis of magnesium chloride. The modified surfaces were not get damaged for operation time exceeding 4 hours while the plain graphite surface could withstand for less than an hour of electrolysis.

Further studies are necessary to characterise the surface film and to optimise the thickness of the modified film. Long-time

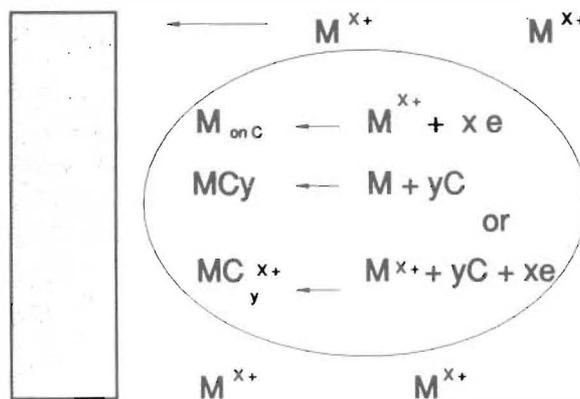


Fig. 4: Scheme of reactions occurring on the graphite surface

TABLE III: Stability of electrodes for electrolysing magnesium chloride at 993 K

Current density A.cm <sup>-2</sup>	Plain graphite*	Modified graphite
0.3	Attack about 1 mm deep	No attack
0.5	Attack about 1 mm deep	No attack
0.7	Attack about 2 mm deep	No attack
1.0	Attack about 2 mm deep	No attack

\* Observation made after half an hour of electrolysis

and bench scale electrolysis studies are needed prior to recommending this electrode for industrial use.

### CONCLUSIONS

The discharge potential studies on the graphite surface in chloride melt containing titanium ions showed the possibilities for the formation of titanium carbide. XRD studies supports the possibility. The modified surface obtained in this study was stable and it could be used as cathodes for electrowinning of metals like magnesium etc.

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