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## **Lab-scale chromium electrowinning in a diaphragm-type cell: effect of anode material and the head between the catholyte and anolyte levels ( $\Delta h$ )**

**Cüneyt Arslan, Sebahattin Gürmen, Fatma Arslan, Ayşe Gamze Onuk Elçin**

Istanbul Technical University, Metallurgical & Materials Engineering Department  
34469 Maslak / Istanbul, Turkey

**Email:** [arslanc@itu.edu.tr](mailto:arslanc@itu.edu.tr)(Cüneyt Arslan), [gurmen@itu.edu.tr](mailto:gurmen@itu.edu.tr) (Sebahattin Gürmen),  
[arslanf@itu.edu.tr](mailto:arslanf@itu.edu.tr) (Fatma Arslan), [a.gamzeonuk@gmail.com](mailto:a.gamzeonuk@gmail.com) (Ayşe Gamze Onuk Elçin)

### **ABSTRACT**

Turkey has a 6% share in the world of chromite mining and ferrochromium is the most important product in exports. The electrowinning of chromium metal follows the dissolution of chromium from chromite or high-carbon ferrochrome after its separation from gangue and metallic impurities. Although ferrochrome was found to be the most expensive starting material, the use of chromite ore is not practical because of the number of processing steps involved. Production of electrolytic chromium for Turkey becomes important because of having large reserves of chromite ores and producing an important amount of ferrochromium in the world. It is also one of the most important strategic and critical materials for nations. In the frame of electrolytic chromium production from domestic resources, laboratory-scale chromium electrolysis was conducted using a diaphragm-type cell. A synthetically prepared

chrome-alum solution and different anode materials, such as pure lead, Pb-Ca-Sn alloy, carbon plate, pressed & sintered graphite, and IrO<sub>2</sub>-coated titanium anode were used. The fixed experimental conditions were: temperature of 52°C, solution pH:2.1, 750 A/m<sup>2</sup> current density, and electrolyte concentrations of 40 g/L Cr and 90 g/L NH<sub>4</sub><sup>+</sup>. Moreover, the head between the catholyte and anolyte levels ( $\Delta h$ ) was also changed to examine its effect on the cathode morphology, which was characterized by the SEM analyses. The dimensionally stable IrO<sub>2</sub>-coated titanium anode was found to be the supreme electrode among those tested, in terms of both giving the lowest cell potential and yielding the least amount of Cr<sup>6+</sup> in the anolyte.

**Keywords:** Chromium, electrowinning, anode material, Cr(VI) concentration

## 1. Introduction

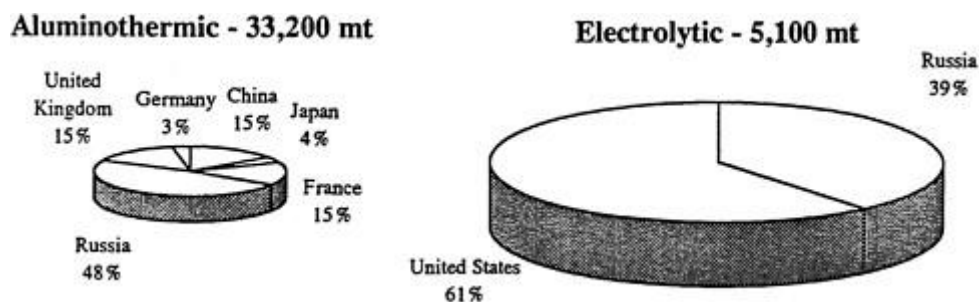
Chromium, a steely gray, lustrous, hard metal that takes a high polish and has a high melting point, is a silvery-white, hard, and bright metal plating on steel and other material. Commonly known as chrome, it is one of the most important and indispensable industrial metals because of its hardness and resistance to corrosion. Therefore, it is used in the areas of metal ceramics, plating, alloys (e.g., stainless steel), dyes and paints, to produce synthetic rubies, to manufacture molds for the firing of bricks, as a catalyst in dyeing and tanning of leather, and in metallurgy to provide corrosion resistance and a shiny finish. Chromium is also vital for good health. Insufficient amounts result in glucose intolerance in humans. Organ meats, mushrooms, wheat germ, and broccoli are all excellent dietary sources of chromium [1].

Chromite ore deposits were created when magma intruded on the earth's crust. Chromite ore deposits are classified by type into stratiform, podiform, and lateritic deposits. Stratiform deposits, indicated by circles, or podiform deposits, indicated by squares, were formed depending on the rate of cooling and subsequent environmental conditions. The distribution of chromite ore deposits shows that economically recoverable resources are geographically concentrated in the Eastern hemisphere [2]. The major deposits are in India, Kazakhstan, and South Africa, all in the Eastern hemisphere. In the Western hemisphere, there are significant producing deposits in Brazil and Cuba. The major producing stratiform chromite ore deposits

are located in southern Africa and India; the major producing podiform deposits are located in Kazakhstan and Turkey.

Turkey has a 6% share in the world of chromite mining and possesses 25 million tons of reserves [3]. Ferrochromium is the most important product in exports. The majority of Turkey's chromite production has been utilized by the ferrochromium industry. In 2017, Turkey ranked second in chromite exports in the world with a share of 10,6%. The most important chromite reserves are located in the Güleman district of Elazığ, the Kopdağ district of Erzincan, the Fethiye district of Köyceğiz, Muğla, Eskişehir, and the Pozantı district of Adana, Harmancık, the Orhanlı district of Bursa, and the Pınarbaşı district of Kayseri. Turkey's total export of chromite was USD 344 million in 2017, with a 41% increase compared to the previous year. Major markets were China, Sweden, Belgium, and Indonesia [3].

Pure chromium is produced either by the thermal reduction of  $\text{Cr}_2\text{O}_3$  with aluminum (aluminothermic method) or by the electrolysis of trivalent chromium solutions. Aluminothermic chromium is a black, silver bright color, metallic luster, containing 98% Cr, according to the use of impurities have different requirements; whereas electrolytic chromium is sheet shape, dark brown surface, after hydrogen refining surface bright, containing 99% Cr [4]. Chromium has a wide range of applications such as in alloying, chemical, and refractory industries. Its high resistance to corrosion and extreme strength make it an optimum metal for use in plating and metal finishing [5,6,7]. Figure 1 shows worldwide production percentages for the major aluminothermic and electrolytic chromium-metal producers [8].



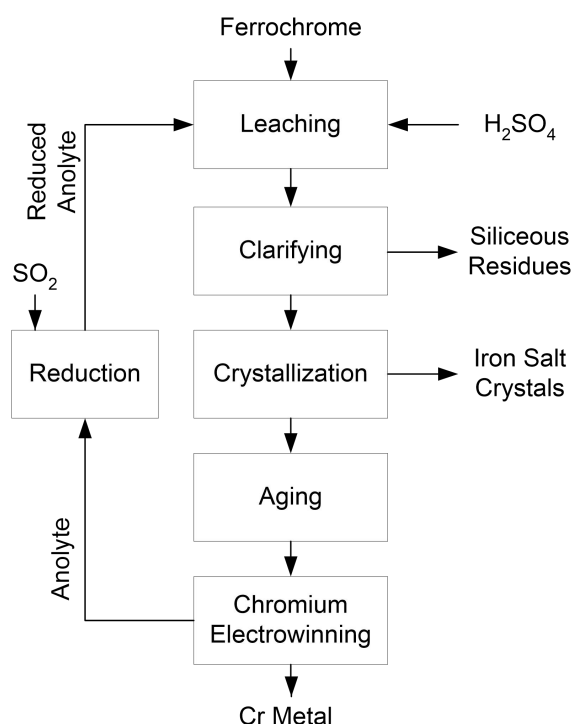
**Figure 1.** Worldwide production percentages for the major aluminothermic and electrolytic chromium-metal producers [8].

## 2. Electrolytic Chromium Production

In 1856, Gunter showed the possibility of electrolytic precipitation of chromium from solutions of chromium anhydride [9]. The first careful investigation of the electrolytic method of producing compact chromium was carried out by Adcock in 1927 [10]. Several works by Nechaeva et al. were devoted to the processes of producing chromium by electrolytic precipitation from solutions of chromic and chromous chloride [11,12,13]. In the nineteen forties, the United States Bureau of Mines (USBM) developed a process for chromium electrowinning from chrome-alum solutions obtained by leaching chromite. It was piloted by the Union Carbide Company and an industrial operation was started in Marietta, Ohio, in 1954.

The main electrolytic method used for the production of large tonnages of chromium metal is the chromium (III) or trivalent chrome-alum bath electrolyte method. Solutions suitable for producing chromium metal can be derived from ore by oxidative roasting in alkali or dissolution of chromite in sulfuric acid. However, the preferred starting material is milled high-carbon ferrochrome that is leached in recycled anolyte and make-up  $\text{H}_2\text{SO}_4$ . A simplified flow sheet showing the essential steps in the process is given in Figure 2. The 20-mesh ferrochrome (67% chromium) is leached at about  $90^\circ\text{C}$  in roughly 3-metric-ton batches without agitation. Approximately 95 percent of the solids dissolve. The hot-acid leach solution is clarified, and the undissolved solids, such as silica, are separated by filtration. The filtrate is cooled using mother liquor from the ferrous ammonium sulfate circuit and the mixture is conditioned at  $80^\circ\text{C}$ , causing the transformation to the green, non-alum form of chromium. Upon further cooling, the crude iron sulfate crystals form, are separated for further conditioning, and are recrystallized as ferrous ammonium sulfate [8].

Chromium electrowinning is a very complex and still poorly understood process. The current efficiency is usually below 50% and strongly depends on pH, temperature, current density, and the presence of impurities in the solution [14]. The current design and operating conditions of chromium electrowinning from a chrome-alum solution are based on the results published by the USBM around the nineteen fifties. The electrowinning of chromium metal follows the dissolution of chromium from chromite or high-carbon ferrochrome after its separation from gangue and metallic impurities. The use of chromite ore in the production of electrolytic chromium is not practical because of the number of processing steps involved [14]. A typical flow sheet, showing the production of metallic chromium from ferrochrome, is given in Figure 2.



**Figure 2.** Flowsheet of electrolytic chromium metal production from ferrochrome [15].

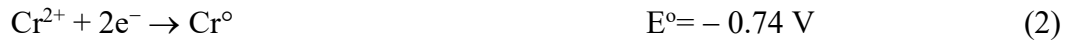
In the electrolytic chromium production process, milled high-carbon ferrochromium is leached by a mixture of reduced anolyte, a chrome alum mother liquor –a solution of ammonium sulfate recycled from a later stage in the process, and sulfuric acid. The resulting slurry is chilled, and silica and other undissolved solids are filtered. The iron forms ferrous ammonium sulfate crystals and is filtered out. The mother liquor is sent back to the leach circuit while the chrome alum crystals are dissolved in hot water and fed into the catholyte chamber of an electrolytic cell. The cell is divided by a diaphragm to prevent the chromic and sulfuric acids formed at the anode from mixing with the catholyte. With the passage of electric current from a lead anode to a stainless steel cathode, chromium is plated onto the cathode. Every 72 hours, deposited chromium metal is stripped from the cathode, sealed in stainless steel cans, and heated to 420°C to remove water and hydrogen. This electrolytic chromium contains 0.5% oxygen, which is too high for some applications; combining it with carbon and heating the briquettes to 1400°C at around  $10^{-4}$  atm lowers the oxygen content to 0.02%, producing metal more than 99.9 percent pure.

Arslan and Duby [16] investigated the factors affecting the anodic processes in the electrowinning of chromium by carrying out electrolysis experiments with chromium ammonium sulfate solution in a laboratory-scale cell of approximately 90 ml equipped with a diaphragm. There was no attempt to optimize the cathodic deposition process. The behavior

of the traditional lead-silver anode was compared with that of two commercially available dimensionally stable anodes. The current efficiency for the anodic oxidation of the chromic ion varied from about 75 to 100% with the lead-silver anode while it was only about 10 to 20% with the dimensionally stable anodes.

The main and side reactions taking place during electrolysis of chromium are summarized as follows [17]:

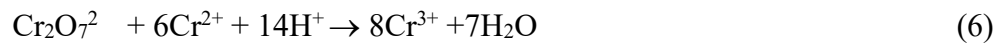
at the cathode:



and at the anode:



$\text{Cr}^{6+}$  ions diffuse through the diaphragm into the catholyte chamber and oxidize  $\text{Cr}^{2+}$  ions back to  $\text{Cr}^{3+}$ :



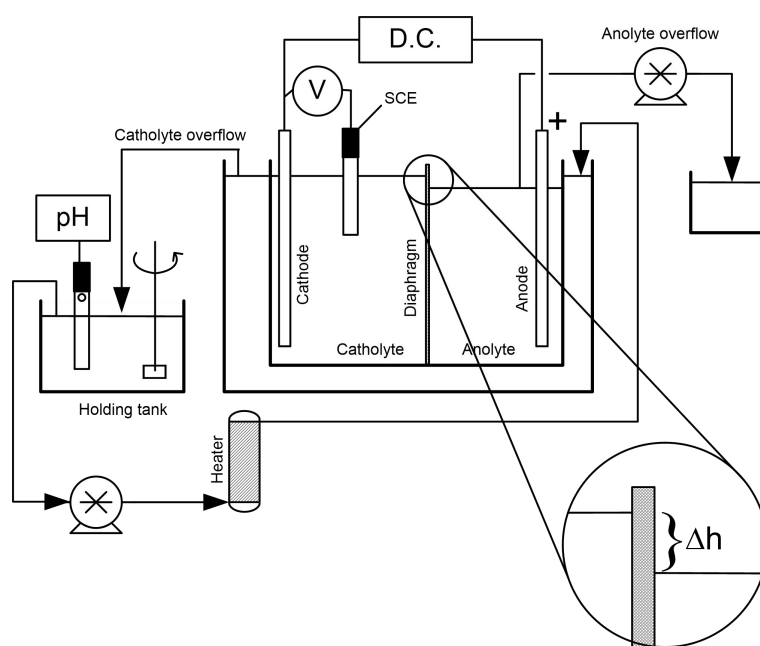
causing a decrease in the net current efficiency for chromium electrodeposition.

Within the last decade, relatively few studies have been conducted to minimize energy consumption in chromium electrowinning, define clearly the electrochemical reactions taking place in the anolyte and catholyte chambers, investigate the effect of diaphragm type on current efficiency, decrease the amount of  $\text{Cr(VI)}$  ions that have a detrimental effect on the electrolysis process, and/or to examine the type and geometrical variety of anode materials which would decrease the cell potential and specific energy consumption [18,16].

In Turkey, there is no electrolytic chromium production, although it is one of the richest countries in the world in terms of chromite reserves and ferrochrome production. Therefore, our country needs to produce metallic chromium from our resources. In the framework of a project created for that purpose, a starting part of it presented here, aimed at investigating the effect of anode material on the cell potential and  $\text{Cr}^{6+}$  concentration in anolyte and the effect of head difference ( $\Delta h$ ) on the morphology of electrolytic chromium deposited at the cathode.

### 3. Experimental

During the experimental work, reagent-grade chromium-III sulfate (made by Alfa), ammonium sulfate,  $\text{H}_2\text{SO}_4$  (made by Merck), and distilled water were used. Chromium and ammonium analyses of the electrolyte were carried out with analysis reagents made by Merck. The electrolyte was fed to the electrolysis cell by a peristaltic pump (made by Ismatec) with an adjustable flow rate and was heated by a Haake D8 thermostat. Another pump (Ismatec) was utilized to keep the anolyte level the same throughout the experiment. A WTW-brand pH meter was used to measure the pH. Konstanter-Gassen brand d.c. source supplied the current. Two digital multimeters measured the individual electrode and total cell voltages. The electrolysis cell, placed into the electrolysis bath, was made of plexiglas<sup>®</sup> and contained two chambers (anolyte and catholyte), separated by the diaphragm. Various anode materials (pure lead, Pb-Ca-Sn alloy, iridium oxide-coated titanium, sintered graphite, and carbon plate) were tested during the experimental study, while stainless steel (SS 316) cathode was utilized throughout. A schematic of the experimental setup is given in Figure 3.



**Figure 3.** Experimental setup (Temperature bath, holding the electrolysis cell, was not shown in order not to complicate the schematics.)

Experiments were conducted under the previously determined [18] optimum conditions: concentrations of 40 g/L  $\text{Cr}^{3+}$ , 90 g/L  $\text{NH}_4^+$  and 350 g/L  $\text{SO}_4^{2-}$ , pH=2.1-2.4, the temperature of  $52 \pm 1^\circ\text{C}$ , and 750  $\text{A/m}^2$  current density. The electrolyte samples were analyzed spectro-

photometrically for their chromium and ammonium content by using a microprocessor-controlled UV-visible spectrophotometer made by Shimadzu. SEM pictures of the cathode surface at the end of electrolysis were also taken.

### 3. Results and discussion

Experimental results are given in two parts; effects of anode material on electrolysis and the level difference between anolyte and catholyte ( $\Delta h$ ).

#### 3.1. Effect of anode material

Figure 4 displays cell voltages recorded during the experiments, conducted at the optimum conditions with  $\Delta h=1.0$  cm and with different anode materials such as pure lead, Pb-Ca-Sn alloy, iridium oxide-coated titanium, sintered graphite, and carbon plate. Although the cell potentials start at different values for different anodes, they eventually coincide at around 4.75 V. The utilization of the IrO<sub>2</sub>-coated Ti anode resulted in the lowest cell potential values, whereas the carbon sheet gave the highest.

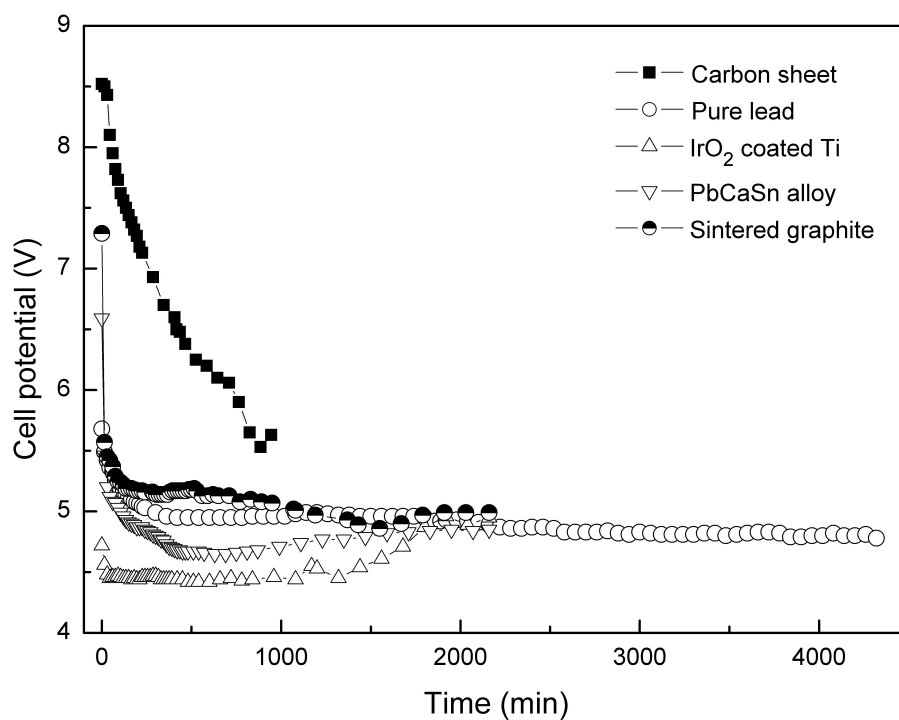
The cathode potentials of these same experiments can be seen in Figure 5. The initial cathode potentials vary between  $-0.5$  and  $-1.3$  V where the lead anode gave the highest initial cathode potential ( $-1.3$  V) while the Pb-Ca-Sn alloy anode gave  $-0.5$  V. Cathode potentials seem to increase with time in all cases, except when the pure lead anode is used.

Figure 6 shows the change in the Cr<sup>6+</sup> concentration of anolyte with time. According to the results, the maximum Cr<sup>6+</sup> concentration of approximately 90 g/L was reached within the first 4 hours when carbon anode was used. The carbon sheet deteriorated very rapidly and had to be taken out of the cell after 12 hours of operation, as it caused contamination of the electrolyte. In this study, the least amount of Cr<sup>6+</sup> (7.6 g/L) was obtained when an iridium oxide-coated titanium anode was used. This value is quite comparable with that of a previous work by Arslan (1991) who used a dimensionally stable anode (Type-N, chemical composition of which was not disclosed by the manufacturer due to proprietary reasons) and found the highest Cr<sup>6+</sup> concentration of anolyte to be a mere 5 g/L. On the other hand, utilization of lead-silver alloy as an anode resulted in high Cr<sup>6+</sup> concentrations in the anolyte (around 25 g/L) at the end of 24 hours [18].

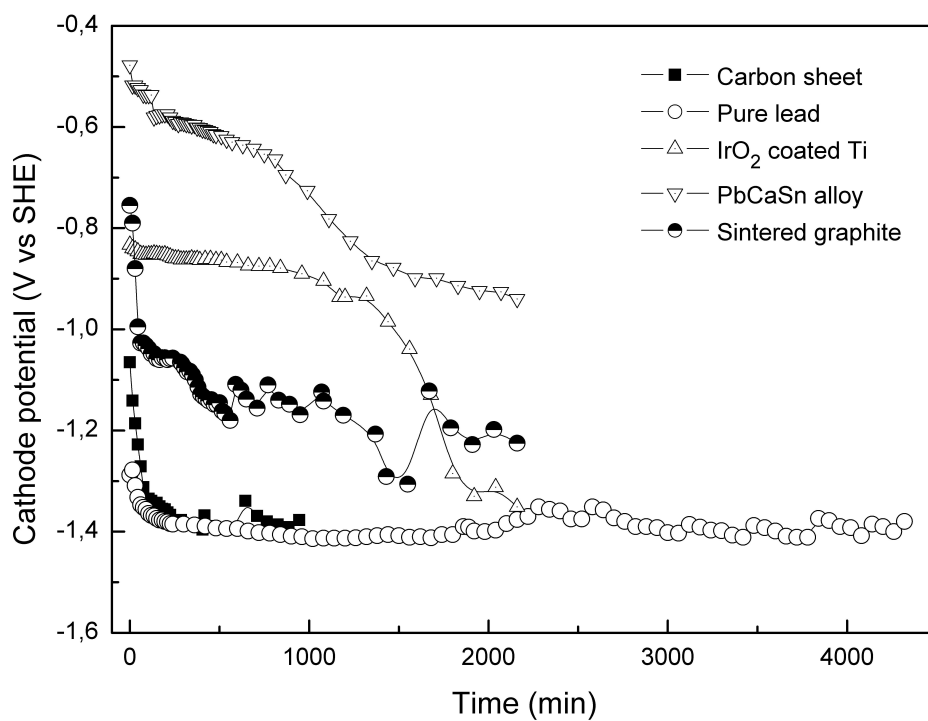
The performance of various types of PbO<sub>2</sub> anodes in chromium electroplating cells has been investigated by Vora et al. [19] revealing that the anode with PbO<sub>2</sub> grown on an anodized lead



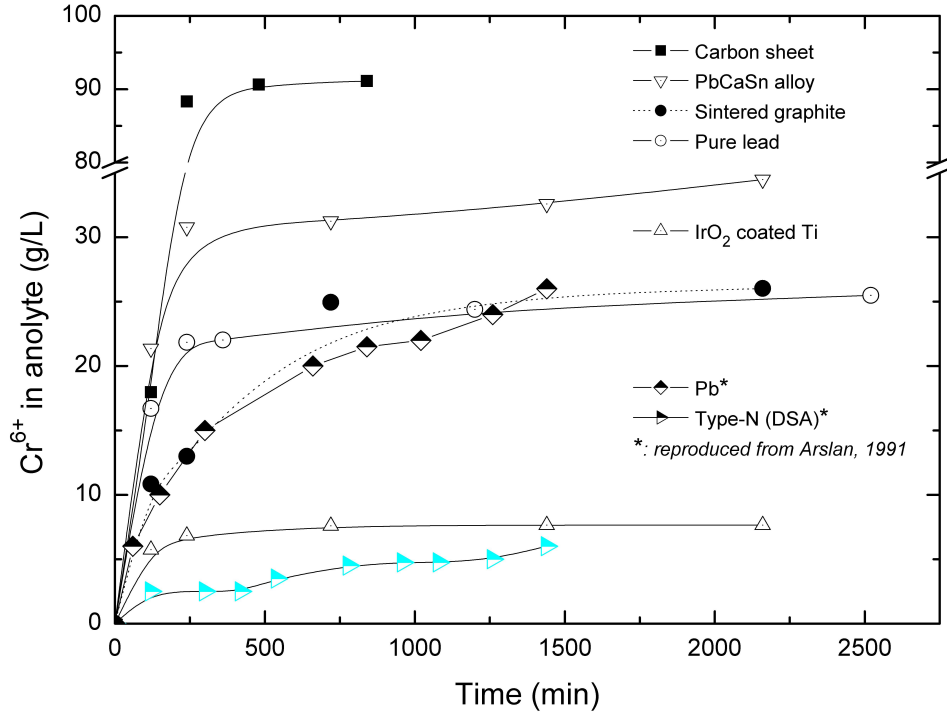
surface as was done in the present study [16], gave the best results in terms of Cr(IV) generation as compared to the electro-deposited PbO<sub>2</sub> on titanium and the battery-grade PbO<sub>2</sub>.



**Figure 4.** Cell potential vs. time



**Figure 5.** Cathode potential vs. time



**Figure 6.** Change in  $\text{Cr}^{6+}$  concentration of anolyte with time

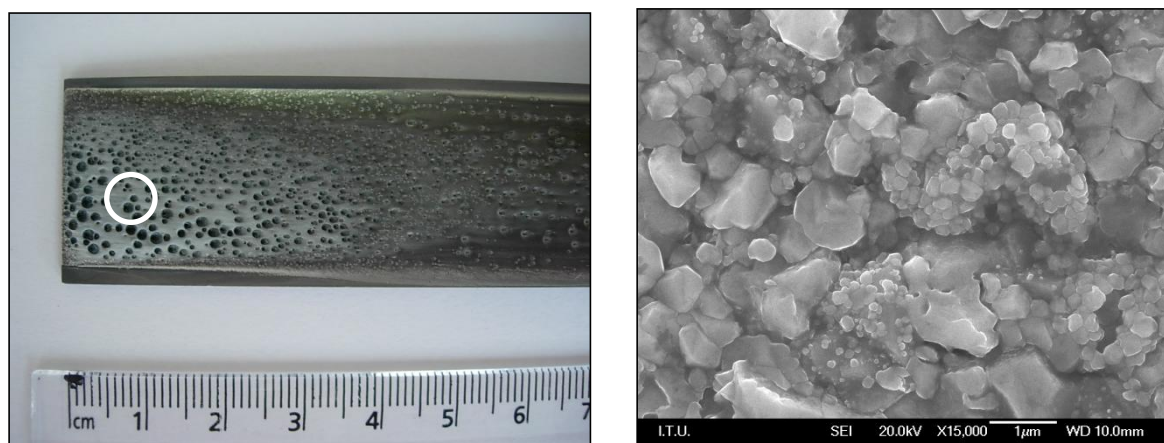
### 3.2. The level difference between anolyte and catholyte ( $\Delta h$ )

Micrographs of the cathodes, obtained at the end of 72 hours with different heads ( $\Delta h$ ), are given in Figures 7 and 8. The hydrogen bubbles formed during the electrolysis create gas pockets on the cathode surface. The upward motion of these bubbles leaves traces behind and thus the quality of chromium metal deteriorates with time. Typical chromium morphology is visible from the SEM micrographs taken from the mid-section of the cathode. When  $\Delta h$  was 0.5 cm, the chromium layer obtained was too thin to peel off from the cathode surface and to take an SEM micrograph. When  $\Delta h$  was 1.0 cm, the chromium layer showed a compact structure and was peeled off easily from the substrate. However, the cathode surface obtained at  $\Delta h=1.5$  cm seems to be more porous in structure, as compared to that of  $\Delta h=1.0$  cm. The morphology of deposited chromium changes from a fine-grained structure to a coarse-grained one when  $\Delta h$  is increased from 1.0 cm to 1.5 cm. Likewise, the number of gas pockets that are visible to the naked eye also decreases with increasing  $\Delta h$ .

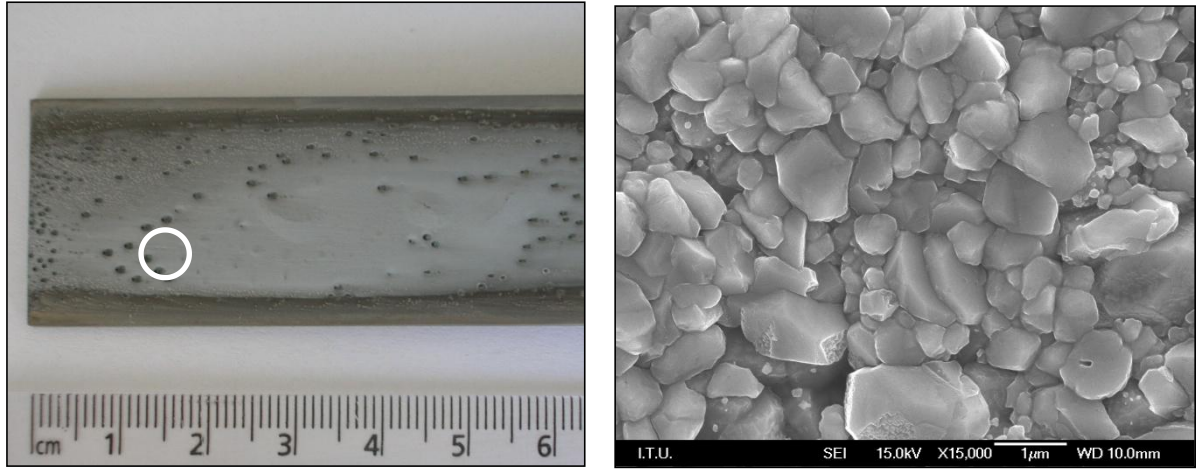
SEM pictures (Figures 7 and 8) of both chromium deposits also show nodular structure where nodule sizes are more uniform in the case of  $\Delta h=1.5$  cm. In the case of  $\Delta h=1.0$  cm, the nodule sizes change in a wide range with no uniformity. According to Kim et al. [20] studies on the effect of electrolysis conditions on hard chromium deposition from trivalent chromium bath, in all bath conditions, the microstructure of chromium deposits has also a nodular structure

with some cracking pattern and nodule size decreased with increasing deposit thickness which increased with electrolysis time. In another study, it was claimed that the metallic chromium obtained is supposed to be in the form of flakes, powder, or nanopowder [21]. Protsenko et al. [22] also found that uniform thick chromium coatings well adhering to a substrate can be produced from the electrolytes based on deep eutectic solvent and the coatings contained inclusions of carbon and oxygen. In another study, changing the deposition parameters in electrolytic chromium deposition (such as temperature and current density) drastically changes the crystalline texture [23]. Production of HC chromium plated on steel at a lower temperature and lower current density exhibited predominately fiber texture. LC chromium plated on steel at a higher temperature and higher current density exhibited an almost random texture. Our study and all studies in the literature show that the chromium deposition morphology changes with electrolysis/electroplating conditions.

Moreover, the maximum  $\text{Cr}^{6+}$  concentration in anolyte was 27.2 g/L at  $\Delta h=1.0$  cm, while it was 36.5 g/L at  $\Delta h=1.5$  cm. As a result of morphological observations and chemical analysis of the anolyte, it was determined that  $\Delta h=1.0$  cm was the optimum similar to the literature findings [16].



**Figure 7.** Cathode surface at the end of 72-hour electrolysis ( $\Delta h=1.0$  cm)



**Figure 8.** Cathode surface at the end of 72-hour electrolysis ( $\Delta h=1.5$  cm)

#### 4. Conclusion

Experiments of chromium electrolysis were conducted to examine the effect of anode material on cell potential and  $\text{Cr}^{6+}$  concentration of anolyte as well as the effect of  $\Delta h$  on cathode morphology. Electrolyte concentrations of 40 g/L  $\text{Cr}^{3+}$ , 90 g/L  $\text{NH}_4^+$  and 350 g/L  $\text{SO}_4^{2-}$ , pH=2.1-2.4, and electrolyte temperature of  $52 \pm 1^\circ\text{C}$  were used in the experiments. It has been found that the head difference between the anolyte and catholyte levels affects the cathode morphology and the  $\text{Cr}^{6+}$  concentration of the anolyte. The morphology of deposited chromium changes from a fine-grained structure to a coarse-grained one when  $\Delta h$  is increased from 1.0 cm to 1.5 cm. Likewise, the number of gas pockets that are visible to the naked eye also decreases with increasing  $\Delta h$ . At a current density of  $750 \text{ A/m}^2$ , cell potential varies between 5 and 10.5 V, when  $\Delta h=0.5$  cm; between 4.7 and 5.7 V, when  $\Delta h=1.0$  cm; and between 4.8 and 11 V, when  $\Delta h=1.5$  cm. Meanwhile, at the same current density, the cathode potential values change between 1248 and 1405 mV, when  $\Delta h=0.5$  cm; between 1278 and 1413 mV, when  $\Delta h=1.0$  cm; and between 1211 and 1479 mV, when  $\Delta h=1.5$  cm. The optimum  $\Delta h$  value is found to be 1.0 cm, at which the least amount of  $\text{Cr}^{6+}$  was formed in the anolyte chamber.  $\text{IrO}_2$ -coated titanium anode gives the lowest cell potential and the least amount of  $\text{Cr}^{6+}$  formation in the anolyte among the electrodes tested.

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