

Compact Anode of Multi-Layer PbO₂ on Titanium used for Electro synthesis of Sodium Perchlorate

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Abstract

Experimental results are presented for the preparation of an electrode to replace platinum in the perchlorate cell. Compact anode of multi-layer lead dioxide on titanium (TSLD) anode has been developed for obtaining a suitable anode size of geometrical electrode shape and type of joining and assembling within the electrochemical cell. This can be considered as a feeding behavior by D.C. current and the suitable quantity of anode electrode to apply cell electrolysis of perchlorate production of high current application.

Current-potential curves of the electrolytic oxidation of chlorate were determined. The polarogram obtained has two potential stages; the lower one is the potential of oxygen evaluation and the higher one is the potential of perchlorate formation which is less than that reported for the platinum anode by 0.3 V.

The prepared TSLD anode has been used successfully in the presence of certain additive (NaF), as a replacement for platinum anode in sodium perchlorate preparation experiments

الخلاصة

تضمن البحث نتائج تحضير قطب بديل لأقطاب البلاتين شائعة الاستخدام من خلايا إنتاج البيركلورات حيث اشتمل العمل تحضير قطب مطور من معدن التيتانيوم المطلية بطبقات متعددة من ثاني أو أكسيد الرصاص وبأبعاد ملائمة للشكل الهندسي للقطب وأسلوب ربطه وتجميعه ضمن الخلايا الكهروكيميائية للأخذ بنظر الاعتبار أسلوب تغذيته بالتيار المستمر وبالمقدار الملائم كقطب أنود لإجراء عملية التحلل الكهربائي لخلايا إنتاج البيركلورات ذات التيار التشغيلي العالي. تم تحديد منحنى الاستقطاب للقطب المحضر في عملية الأكسدة الكتروليتية، ويتضمن المنحنى المستخرج مرحلتين، الأولى تمثل جهد تحرر غاز الأوكسجين أما المرحلة الثانية فتتمثل جهد تكون البيركلورات والتي كانت بقيمة أدنى من جهد تكون البيركلورات باستخدام أقطاب من البلاتين وبمقدار 0.3 فولت. تم استخدام قطب التيتانيوم المطلية بثاني أو أكسيد الرصاص المحضر بنجاح وبوجود مضافات محددة (NaF) كبديل لقطب البلاتين في تجارب تحضير بيركلورات الصوديوم في دراسات لاحقة.

1. Introduction

Lead dioxide is an important electrode material due to its stability under aggressive conditions, high electronic conductivity and low cost of material. It has been used to make anodes suitable for the preparation of sodium perchlorate from sodium chlorate. This type of anode has been used successfully in the presence of certain addition agents as replacement for platinum anode.

By utilizing these characteristics, block lead dioxide electrodes were practically used in the 1940. The electrode being used was formed by cutting a pot-form iron having a lead dioxide-layer on the inside surface thereof by electro deposition ^[1].

The production thereof was very troublesome, and the production yield was bad, such an electrode had brittleness specifically to ceramics, and the specific gravity thereof was about 9, which was larger than that of iron, whereby the electrode was difficult to handle. Hence, the usable ranges of the electrodes were limited ^[1]. The high cost of platinum has prompted for several attempts to replace this metal by cheaper materials ^[2]. Several practical techniques show a strong continuing interest in lead dioxide anodes and their used in electrochemical oxidation ^[3].

A light-weight and durable lead dioxide electrode composed of the combination of titanium and lead dioxide has been produced, that is an electrode composed of a titanium core having electrodeposited lead dioxide on the surface thereof. However, in the electrode, the interface between titanium as the core material and the lead dioxide layer was passivated by the strong oxidative power of lead dioxide, which sometimes resulted in making the passage of electric current impossible ^[4], so electrically conductive titanium could not be used as the electrically conductive member, the lead dioxide layer itself was first used as the electrically conductive member.

For preventing the passivation of the titanium metal substrate by PbO_2 layer, there have been many proposals relating to coating a lead oxide layer on a metal substrate by means of various primary layers ^[5], such as platinum plating or semi-conductive oxides plating to the whole surface of the titanium ^[6].

On the other hand, since the electrodeposition thickness of the lead dioxide layer on the surface of the core material was from 100 to 1000 μ m, which was thicker than the thickness of ordinary plating, the problem of peeling-off the coating by the electrodeposition strain could not be avoided. However, the problem is being solved by laminating or mixing α - lead dioxide and β -lead dioxide ^[7].

The object of this research is to provide a titanium-substrate lead dioxide anode having a long life time and satisfactory stability and having PbO_2 coatings formed on a metal substrate which are dense and excellent in the bondability and shows less internal strain due to electro depositions, which comprises a primary layer comprising semiconductor metal oxide, an intermediate layer comprising α - PbO_2 and a coating layer comprising β - PbO_2 successively coated on substrate comprising titanium metal.

2. Experimental Work

Titanium of commercial purity (ASTM grade B-265) is used as a metal substrate which forms the base component of the electrode is an electro-conductive material having sufficient mechanical strength to serve as support for the coatings and should have high resistance to corrosion when exposed to the interior environment of an electrolytic cell, since a relatively thick layer of lead dioxide is subsequently coated on the substrate, it is preferred to apply a roughing treatment to the surface thereby increasing the deposition area.

A primary layer is formed on the surface of thus prepared titanium metal substrate for protecting the substrate from oxidation during the PbO_2 electrodeposition, and improving the bondability with the $\alpha\text{-PbO}_2$ intermediate layer. The primary layer is formed by using semiconductor oxides such as RuO_2 and TiO_2 (mole ratio 1/2) in the form of HCl acidified butanol solution of ruthenium chloride and tetrabutyl titanate^[5]. For forming such a primary layer, heat decomposing is used. A suitable coating thickness of the primary layer is about 1-2 μm , is obtained.

The $\alpha\text{-PbO}_2$ mainly serves as a joint between the primary layer and the $\beta\text{-PbO}_2$ coating layer, since the $\alpha\text{-PbO}_2$ layer is slightly inferior to the $\beta\text{-PbO}_2$ layer in corrosion resistance and electrical conductivity, excels in ability to adhere to the substrate^[8]. The proper thickness of the α -lead dioxide layer is from 100 to 200 μm . The intermediate layer coating of a desired thickness can be obtained under typical conditions of using an electrolyte in which lead monoxide (PbO) is dissolved to saturation in an aqueous solution of 5N NaOH and electrolysis is conducted with a current density of one Amp/dm^2 and at room temperature. Consequently a rigid purplish black layer of lead dioxide is deposited^[9,10]. The $\beta\text{-PbO}_2$ layer has an extremely satisfactory affinity with the $\alpha\text{-PbO}_2$ intermediate layer.

The $\beta\text{-PbO}_2$ layer is formed by electrolytic process as shown in **Fig.(1)** using an acidic bath containing lead ions, such as an aqueous 30-35% lead nitrate solution, as the electrolyte and using a substrate coated with the primary layer and the intermediate layer as the anode [11,12].

Suitable current density is about 1-2 Amp/dm^2 and at temperature of about (50 to 60 $^\circ\text{C}$), the electrodeposition liquid is desired to be used in a fluidic state. The spent liquid emanating from the electro deposition bath may desirably be received in a neutralizing vessel to be completely neutralized with lead carbonate or lead hydroxide and returned back to the electro deposition bath for reuse. $\beta\text{-PbO}_2$ layer is desired to have a thickness in the range between (200-500 μm).

The electrodeposited $\beta\text{-PbO}_2$ layer has a purplish black color surface flecked with fine particles, compact in texture, and enjoys a higher degree of fastness than the $\alpha\text{-PbO}_2$ layer. The prepared compact anode of multi-layer PbO_2 on titanium is tested to evaluate the performance in electrosynthesis of sodium perchlorate.

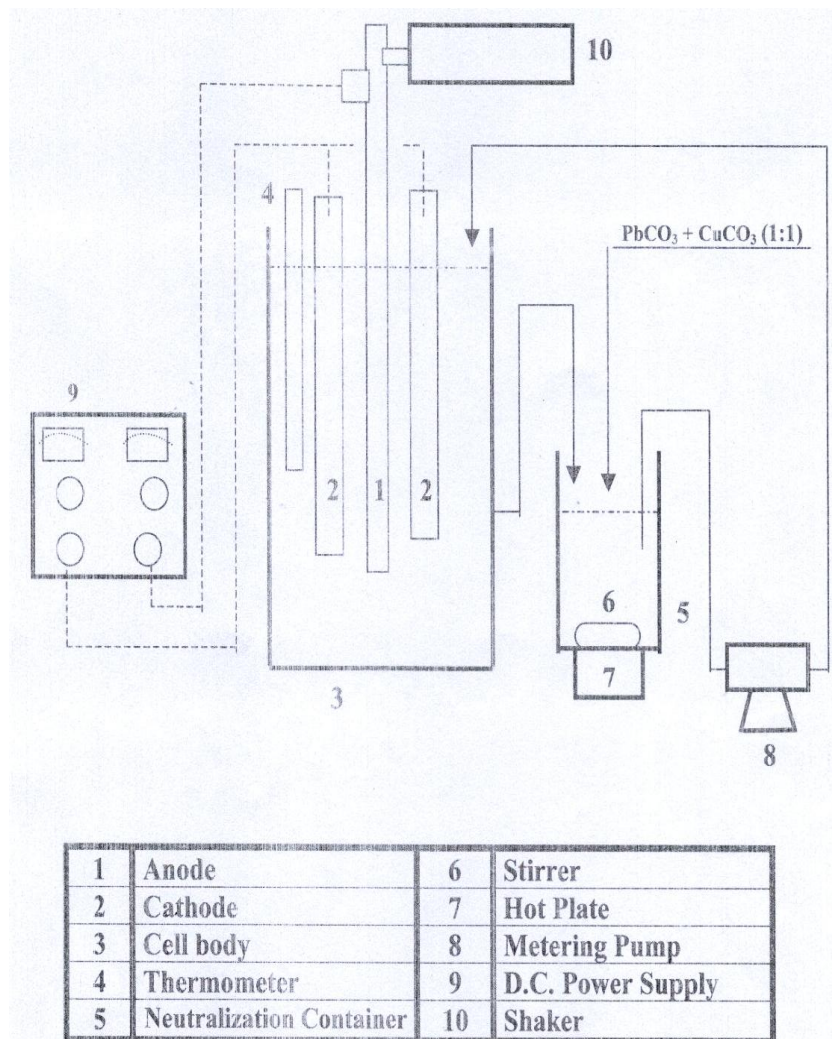


Figure (1) Flow Diagram for the Production of TSLD Anodes

3. Result and Discussion

3-1 Preparation of (TSLD) Anode

The conditions for preparation of $\text{PbO}_2/\text{(Ti)}$ electrode were established as a result of deposition of $\alpha\text{-PbO}_2$, then $\beta\text{-PbO}_2$, on titanium substrates coated with valve metals oxides, from Pb^{+2} (plumbite) solution of different compositions, current densities and different temperatures...etc.

The PbO_2 (Ti) electrode consisting of 150 μm thick $\alpha\text{-PbO}_2$ and 300 μm thick $\beta\text{-PbO}_2$ layers, prepared under these favorable conditions with strong adhesion to titanium substrate and good cohesion within the coating was compact and pin-hole free deposit. The PbO_2 layers did not peel off when the electrode was used for anodic perchlorate production, for more than 400hr of operation in further studied later.

Prepared titanium substrate lead dioxide (TSLD) anodes have many distinct advantages over the other type of PbO_2 anode. This due to the low density of substrate material

4.5gm/cm³ compared with PbO₂ density of 9gm/cc^[8]. And its good mechanical and chemical properties with a thin (1mm) modified multi-layers coating of PbO₂, compared with the thickness required for other PbO₂ layer plated such as 5mm for PbO₂ coating layer on graphite^[2], or 8-16 mm for pure lead dioxide or other coating PbO₂^[4].

The important factors of anode electrode specification are high strength and light (possible achievement for it will be lower thickness). This can be followed by higher active surface area with less mass of anode electrode material used. It can be concluded that titanium substrate lead dioxide (TSLD) anodes prepared have been distinct advantages over the other type of PbO₂ anode, such as increase in anode surface to volume ratio permitting construction of a more compact cell, anode reusability of the titanium substrate at the end of anode life.

3-2 Characterization of TSLD Electrode

3-2-1 Anode Potential

The current vs. potential curves of perchlorate formation was measured using the prepared PbO₂ (Ti) anode, as shown in **Fig.(2)**. When the chlorate solution concentration of 5.6 moles and of pH 7-8 were used; the curve had two potential stages, the lower stage was found to be the potential of oxygen evolution and the second stage which corresponded to perchlorate formation.

On other hand, the curve showed a steep increase of current at around 1.9V (vs. SCE) and was observed as a simple exponential relationship.

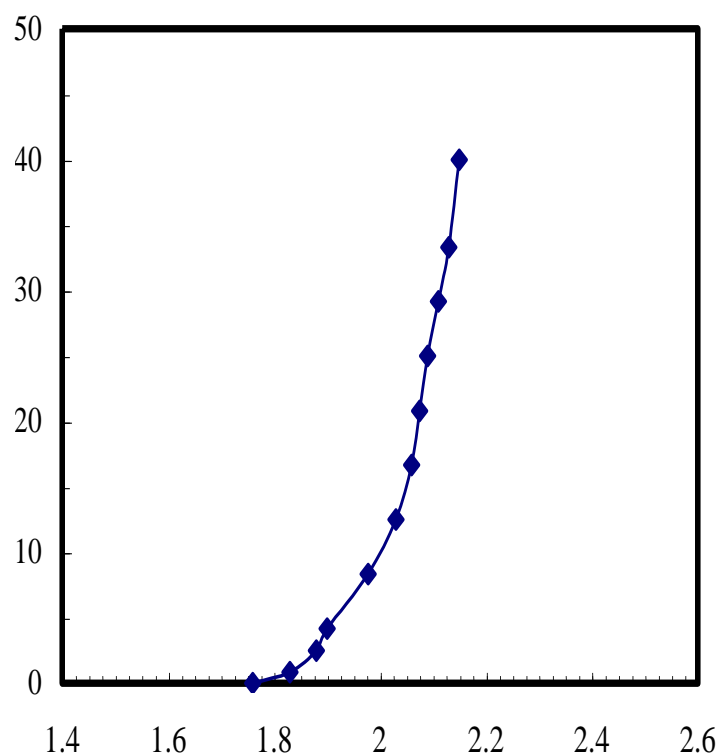


Figure (2) Current Density as a Function of Anode Potential using PbO₂ (Ti) Anode

The current vs. Potential curve for the anodic process of chlorate at platinum was investigated, by Sugino et. al. ^[13], and confirmed by Osuga et. al. ^[14]. They investigated the correlation between anode potential and current density as shown in **Fig.(3)**. In the first or lower stage, the potential range is between 1.5 and 1.7 V; the second, or higher stage, it is higher than 2.1 V (vs. SCE).

From comparison between these two curves, it was found that the potential at which the current corresponding to perchlorate formation began to flow using prepared PbO₂ (Ti) anode was (about 0.3V) lower than that at the platinum anode in almost the same condition.

The above results are much better, compared with the value of 0.25 volts, had obtained by Osuga et. al. ^[14], using pure lead dioxide anode. In addition, the increase of anode potential with increasing current density was very small, but at the platinum anode, the potential increased steadily with the increase of current density.

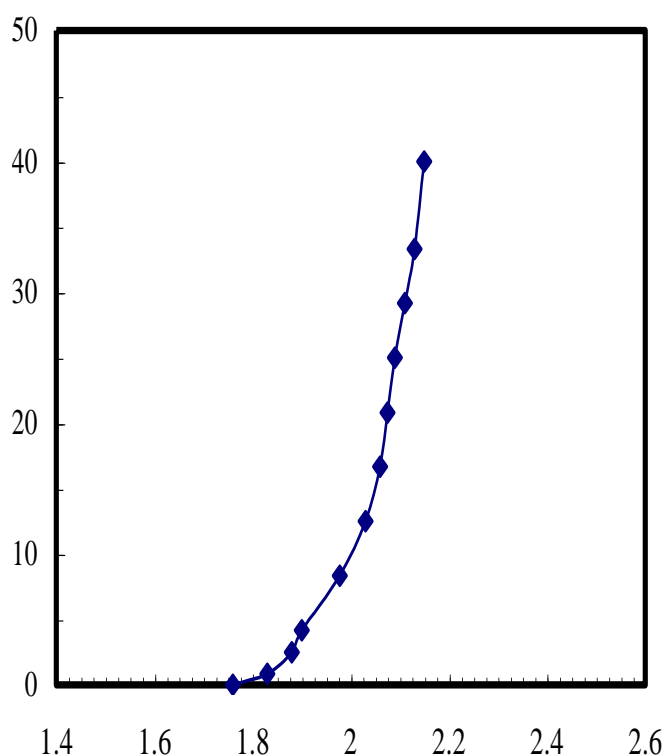


Figure (3) Current Density as a Function of Anode Potential using Platinum Anode as Obtained by Sugino et. al. ^[13] and Osuga et. al. ^[14]

3-2-2 Current Efficiency

The effect of current density on current efficiency was studied in the range of 10 Amp./dm² to 60 A./dm² under alkaline conditions of electrolysis and at 40°C, the results are shown in **Fig.(4)**.

Figure (4) shows the strong dependence of chlorate conversion efficiency on current density, it is noticed that the current efficiency appears to be definitely low at current densities lower than 15 A/dm² at a higher current density between 15-40 A/dm², the current efficiency is slightly increased and this is accompanied by a slight decline in current efficiency.

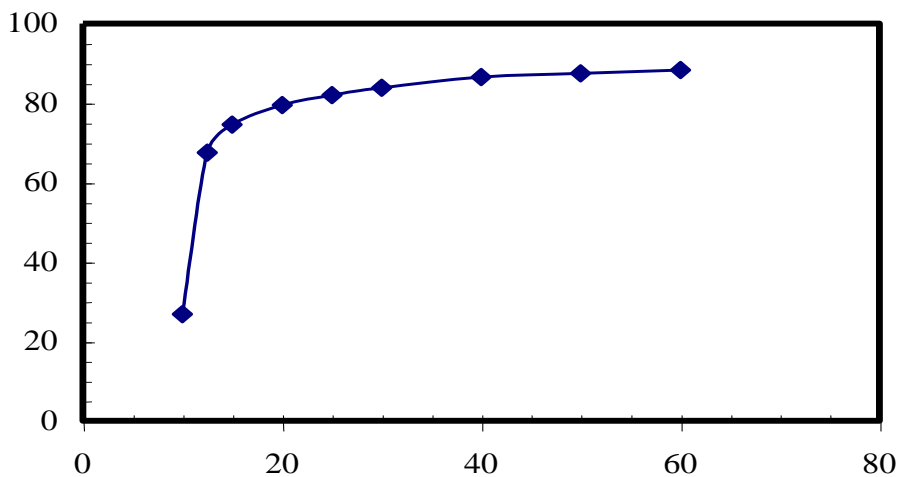
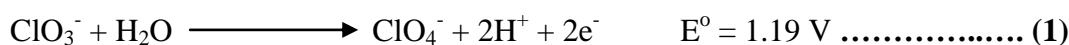


Figure (4) Current Efficiency as a Function of Current Density

Figure (5) shows the increasing in cell voltage with increasing anodic current density with a sharp change between 10-15 A/dm² and lower increase rate between 50-60 A/dm². The above results can be explained as follows:

Since, only the main two over-all reaction ClO₃⁻ oxidation and O₂ evolution take place at the anode with complementary current efficiencies, it is possible to work out both reaction rates as a function of anode potential. The over-all oxidation reactions of anodic chlorate and water at pH equal zero are ^[15]:



At low current densities (lower than 15Amp/dm²), the anode potential does not attain a value high enough for the perchlorate formation to occur at an appreciable rate so that the current efficiency is low (lower than 75%). At higher current density (between 15-40 Amp/dm²), the anode potential is increased and this is accompanied by a slight decline in current efficiency, 75-87% respectively.

The current efficiency (87-88 %) is almost independent of the current density employed in the range 40-60Amp/dm². These results are in agreement with Ode Nora, et. al. ^[15].

A remarkable increase of cell-voltage at a current density more than 50 Amp./dm² to be noted especially from the point of view of cell design and conditions for commercial scale, as shown in **Fig.(5)**.

From the above results, it can be concluded to obtain the optimum current density of electrolysis for perchlorate formation. This can be given as follows, current density between 40-50 Amp/dm² and alkaline condition gives current efficiency 87-87.5% using HClO₄ for acidity adjustment.

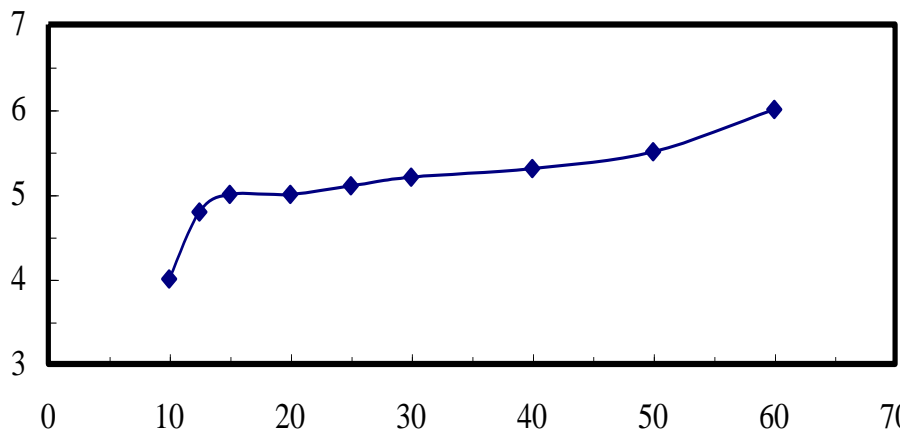


Figure (5) Voltage Drop across the Cell vs. Current Density

4. Conclusions

1. Titanium substrate lead dioxide (TSLD) anodes prepared have many distinct advantages over the other type of PbO₂ anode, such as increase in anode surface to volume ratio permitting construction of a more compact cell, and reusability of the titanium substrate at the end of anode life.
2. It was found that the potential at which the current corresponding to perchlorate formation began to flow was at a round 1.8-1.9 V (vs. SCE), which is lower than that at the platinum anode in the same concentration by about 0.3 V. It is the main reason for the smaller cell voltage than that at the platinum cell.
3. Lead dioxide anode produces sodium perchlorate at a high current efficiency of 75-87.5%.
4. The optimum current efficiency of 87-87.5% obtained at current density between 40-50 Amp./dm² at alkaline conditions, using NaF as additive.

5. References

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