

Influence of F-PbO₂ Doping on the Microstructure, Surface Morphology and Electrochemical Properties of the Electrode for Chlorates Production Cell

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Abstract Electrode fabricated from graphite felts as basic substrate was doped by lead dioxide (PbO₂) and fluorine F⁻ ion through the potentiostatic anode co-deposition method. The fluorine content on the layer controlled and optimized by adjusting different co-deposition potential. The influence of fluorine F⁻ ion on the composition, surface morphology and electrochemical properties of the lead dioxide electrode was characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray detector (EDX), X-ray Photoelectron Spectroscopy (XPS). Electrochemical experiments of Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV) and durability was executed by electrochemical workstation which showed good activity and service life durability. Oxidizing electrolyte of sodium chlorate as one field of application, showed the electrode with optimized content of F⁻ has better performance than that without doped at preferred condition ranged to PH 6.5, temperature 55^oC and 4V constant potential. This investigation can contribute to the improvement of electrochemical cells that may use this material as an electrode. Choosing practical graphite substrate added value to improvement of the electric conductivity. The surface modified of the electrode enlarged its area from limited smoothing to octahedral surface due to the shape obtained from the doping.

Keywords lead dioxide electrode, potentiostatic method, electrochemical properties, oxygen evolution potential.

I. INTRODUCTION

The graphite felts substrate lead dioxide (C-Felts/PbO₂) as anode material of desired chlorates have been widely used in waste water treatment[1],[2] ozone evolution and chemical sources[3] because of its high oxygen evolution potential[4], low cost, excellent conductivity[5] and simple preparation method, specially the stability in acidic environment.[6]

How to improve the electrocatalytic activity and surface life of the lead dioxide anode has been a

research hotspot challenge in modern electrochemical industries.[7]The improvement of electrode performance can raise production efficiency and reduce equipment investment.[8]-[10] approach of consideration to accidents, events and count the existed potential hazards was planned. Research is focused on three basic ways to achieve above goal and controlling the hazards associated with electrolytic cell and its system. First is to think a lot of about the chemical process disadvantages especially the hazards associated with the sensitive input raw materials and hazards that are utilized of the operation variables.[11] Major review of the subjected area which can be intensified, minimized, alternated or substituted and eliminated.[12]-[14] Second way decision could be formed to improve procedure controlling the hazards of the anode reactions through modifications, installing additional safety interlocks or adds systems such as mixing and filtering. Third way, improving emergency responses by controlling some measures aimed to passive, active or enhance procedural operation.[15]

Researchers reported that the F⁻ doping into the PbO₂ electrode mainly has great effect on microstructure, surface morphology, physical and chemical properties, due to synergistic effect between the elements. The discussion of Pb²⁺ and F⁻ co-deposition will lead to further understand the effect of F⁻ doping on the PbO₂ electrode performance.[16]-[18]

Designation of chemical process intends to avoiding accumulation of hazards exist in the field of chlorate production “corresponding high current, long term of continuous process, different materials structure and to save electrocurrent path”,[19],[20] all requirements could drive the object of the paper will be formulated.[21]-[23] The method of deposition aims to notable key processes of generating desire molecules[24],[25] through following the potential of oxygen evolution reactions (OER).[26]

II. EXPERIMENTAL

Graphite (C-Felts), Pb(NO₃)₂, NaF, HNO₃, Na₂SO₄, NaClO₃ and other related chemical reagents

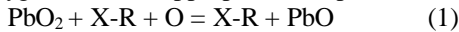
were of analytical grade. All solutions were prepared with doubly distilled water.

A. Preparations of Electrodes

Graphite felts substrate (geometric size 20x20x1 mm), F- PbO₂ film electrode was prepared by anode co-deposition, the electrodeposition solution consisted of 0.1 mol/L Pb(NO₃)₂, 0.01 mol/L NaF and 0.1 mol/L HNO₃. Pb(NO₃)₂ provides Pb⁺² for PbO₂, NaF provides F⁻ for F-doped PbO₂ and HNO₃ was used to adjust PH of the electrodeposition solution.

Potentiostatic depositing was carried out at temperature 70 °C for 1hr. In this paper 1.45 V, 1.50V, 1.55V and 1.60V of deposition tuning potentials were selected respectively. During the electrodeposition, the electrolytic cell with fourth electrodes was employed, the volume was 100ml. The prepared electrode of F-doped PbO₂ was served as a working electrode (WE) with geometric area (20x20) mm, more over saturated KCl salt bridge, standard calomel electrode (SCE) was served as a reference electrode (RE). Accordingly, the potential mentioned in this paper are all referred to SCE. The current efficiency of lead dioxide formation is taken 95%, 94%, 34%, 12% at 1.45V, 1.50V, 1.55V and 1.60V, respectively. For free fluorine F-depositing solution current efficiency is taken 45% at 1.55V. All experiments were performed at temperature (70±1°C). The potential control was carried out by electrochemical working station (Parastat 2273 Ametek made in USA).

There are a number of anode reactions that involve the introduction of oxygen into the electroactive species and that are almost unique to fluorine lead dioxide as an anode material. These include both inorganic (e.g., the conversion of chlorate to perchlorate). Typically the current efficiency at fluorine lead dioxide anode is 35 -100% (some oxygen is also evolved) and no more than a few percent at electron-transfer electrodes such as graphite. Although it is not implied that all reactions at PbO₂ occur by such mechanisms, it is tempting to propose that it is possible for the lead dioxide surface to transfer oxygen atoms to appropriate acceptors, i.e.



More generally, the electrochemistry of lead dioxide electrodes has been reviewed. Traditionally, lead dioxide anodes have been prepared in situ by anodizing lead, usually in a sulfuric acid medium. More recently, there has been considerable effort to develop procedures for making high-quality and long-life PbO₂ on carbon and titanium.[27],[28]

B. Characterizations of Composition, Microstructure, Morphology and Electrochemical Performance

The microstructure of the film electrode was detected with XRD using a Rigaku diffractometer (Japan) with Cu k α-radiation source operating at 40.0 kV and 200.0 mA .The valence and content analysis of

Pb and F were carried out by XPS using type ESCALAB 250, ThermoFisher Scientific USA, X-ray Source Monochromated Al Kα 150W, Spot size 500µm, Pass Energy 200eV for survey; 30eV for high resolution scans, Lens Mode -Large Area XL.The morphology and ratio of elements content was examined with a SEM (Carl Zeiss Jena-ZEISS) and EDX respectively.

The electrochemical properties of PbO₂ electrode with different doping content of F⁻ were characterized by linear Scanning Voltammetry (electrochemical working station Parstat 2273, Ametek) at scan rate of 5mV.s⁻¹. The electrolytic cell with fourth electrodes was employed, the prepared F-PbO₂ electrode was served as a working electrode (the geometric area:20x20mm) a Ti/Ru was a counter electrode and a SCE was a reference electrode. The electrolyte used was an aqueous solution of 0.5mol/L Na₂SO₄.

Bulk anodic oxidation of Sodium chlorate 100g/INaClO₃ was carried out using an electrolytic cell with a single compartment without diaphragm. The anodes were F-PbO₂ electrodes and free-doped PbO₂ electrode, with 4cm² area, the cathode was Ti/Ru oxide with area 4cm² and an interelectrode gap of 20mm. Electrolysis at different constant voltages (3V, 3.5V and 4V) was optimized using 8511 (potentiostatic/ galvanostat-Eternal Electrochemical Company ,China).The electrolyte was 100ml and it was stirred by magnetic stirrer, 0.5mol/L Na₂SO₄ was used as the supporting electrolyte , and the PH value of the solution was adjusted to 2 , the temperature was controlled at (70±1°C) and time 30 hour.

III. RESULTS AND DISCUSSION

A. Effect of F- doping on the composition

Figure 1(I) shows a model of the PbO₂ surface adopted cluster structure, according to XPS data for PbO₂ which was deposited from nitric acid solutions in the presence of 0.02 M NaF, the fluoride content in the oxide bulk was about 4 at %. For the conditions that give a uniform distribution of fluoride within the PbO₂ layer with Θ_{OH} + Θ_F =1, the average surface coverage by fluoride was calculated to be about 6%.[23],[28] In our simulation of fluorine doped on PbO₂, two OH ions are replaced by two fluorine ions (Fig. 1(II)) Cluster suggest that the effect of the fluorine doped is mainly that of changing the surface coverage of adsorbed oxygen species.

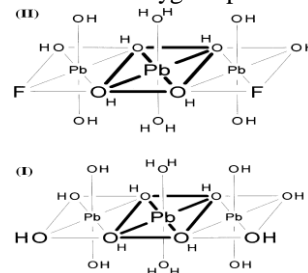


Fig. 1 shows an example of models of Oxygen substitution with Fluorine.

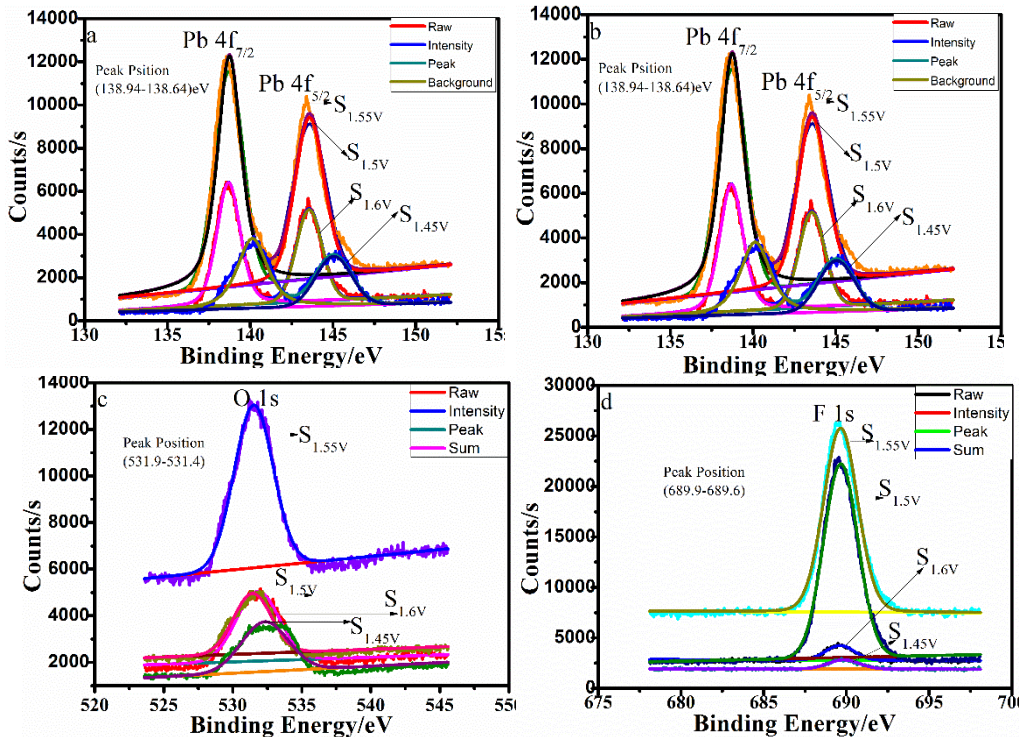


Fig.2 a, shows XPS spectra of the F-PbO₂ electrode prepared under different deposited potentials, S_{1.45V}, S_{1.5V}, S_{1.55V}, S_{1.6V}; b, c and d are showed scanning of XPS spectra of elements Pb, O and F in the F-PbO₂ electrode.

However, despite the limitations, the above conclusion on the importance of changes in the surface coverage of oxygen species is supported by the XPS data. In Fig. 2 the XPS spectra in the O1s region shows that F-doping causes a marked decrease of the broad signal at the higher binding energies which attributed to adsorbed OH and H₂O see atypical XPS spectrum of F-doped PbO₂ electrode prepared under different deposition potentials. The valence state of Pb is judged by Pb4f 7/2 spectrum. If the electron binding energy is between 138.937eV to 138.685eV excluding S_{1.45V} the valence of Pb can be assigned to quadrivalent (IV). as shown in figure 2b, the four prepared electrode materials display conformably high intensity Pb4f 7/2 spectrum peak around the 138.81eV, indicating that Pb mainly exist in the form of Pb (IV) inside the electrode. The electron binding energy of O1s in ionic state (O²⁻) was at about 531.6eV, so the peak in figure 2c illuminate that O inside the electrode was chemical combination with Pb in ionic state (O²⁻), the characteristic peaks appearing at 531.796-531.423eV. In figure 2d displayed that the F⁻ substituted oxygen ions in the oxide lattice.

Figure 3 shows EDX graph, the atomic ratio Pb to F in the F-doped electrode prepared under different deposition potentials which summarized in table 1.

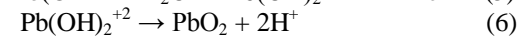
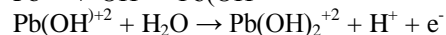
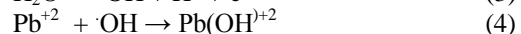
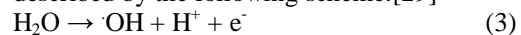
Thus, the doping percentage of the F⁻ in the PbO₂ electrode is closely related with deposition potential, namely, the different atomic ratio of Pb to F in the PbO₂ electrode can be obtained through changing the deposition potential. From table 1, it is noted that when the deposition is 1.60V, the doping content of F is lowest one, the atomic ratio of F to Pb is only 0.089:0.89; when the deposition potential is 1.50V, the

doping content of F increases significantly, the atomic ratio of F to Pb reach the maximum of 0.86:1.19; when the deposition potential reduces to 1.45 V, the doping content of the F also decreases, the atomic ratio of F to Pb equal to 0.23:1.5 and for 1.55V equal to 0.15:4.5.

TABLE 1. ATOMIC RATIO OF F TO Pb IN THE F-PbO₂ ELECTRODES PREPARED UNDER DIFFERENT DEPOSITION POTENTIALS

Sample	Plating solution (mol/L)	Deposited potential (V)	Atomic ratio (F:O:Pb:)
S _{1.45V}	0.1MPb(NO ₃) ₂ +0.02M NaF+0.1M HNO ₃	1.45	0.23:1.68:1.5
S _{1.50V}	Ibid	1.50	0.86:1.62:1.2
S _{1.55V}	Ibid	1.55	0.15:1.84:4.5
S _{1.60V}	Ibid	1.60	0.09:1.14:0.9
S _{Free.1.55V}	0.1MPb(NO ₃) ₂ ,0.1M HNO ₃	1.50	-----

The change shows that the doping content of fluorine ion F⁻ in the PbO₂ structure and electrode film does not always monotonously increase with decreasing deposition potential, whereas there is maximum value at the potential of 1.50V, the presence of F ionic additives in the electrodeposition solution causes only slight shift in the electrodeposition rate of PbO₂ without seemingly changing the deposition mechanism, which was described by the following scheme.[29]



During the electrodeposition process, parts of the OH groups were substituted by F⁻, having a similar ionic radius.

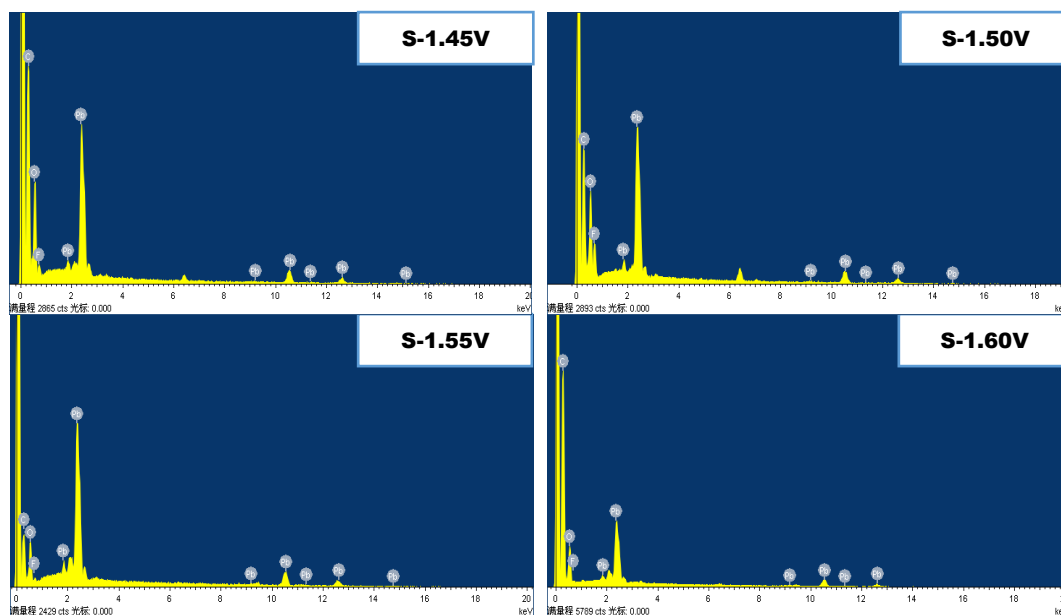


Fig.3 Energy Dispersive X-ray Detector(EDX) of the optimized F-PbO₂ electrodes prepared under different deposited potentials, S_{1.45V}, S_{1.5V}, S_{1.55V}, S_{1.6V} shows species ratio of Pb,O and F basic measures refer to standard compounds PbF₂,NaAlSi₃O₈ and MgF₂ respectively. The substitution percentage of F in the PbO₂ electrodes is closely related with deposition potential.

B. Effect of F- doping on the microstructure

Crystallography Structure characterized by X-Ray Diffraction (XRD) spectra of the F-doping electrode, illustrations with different doping content of F⁻ (S_{1.45V}, S_{1.5V}, S_{1.55V}, S_{1.6V}) are shown in figures 4. The composition and structure of the electrode materials change with electrodeposition potential. The composition of electrodeposition solution of above samples is identical.

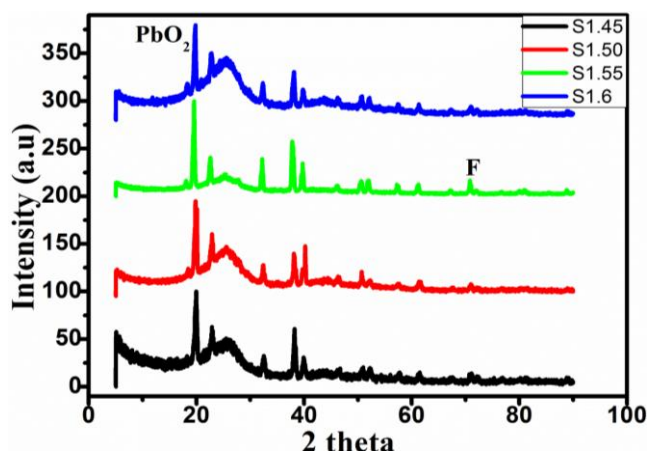


Fig.4 XRD spectra of the F-PbO₂ electrodes prepared under different deposited potentials, S_{1.45V}, S_{1.5V}, S_{1.55V}, S_{1.6V}

The presence of PbF₂ crystals in figures 4 is the most direct expression of co-deposition of Pb⁺² with F⁻ onto the electrode surface. As well all know, F⁻ is smallest anion and only carry one charge; therefore, it is migration rate is very fast. Moreover the solubility of PbF₂ (solubility product constant K_{sp} = 3.7x10⁻⁸) [30] is far less than Pb(NO₃)₂. Thus the conditions all

favor the F⁻ co-deposition with Pb⁺² to form PbF₂ crystals. The conductivity of PbF₂ (1.0x10³-1.0x10⁴ S.cm) is higher by about one order of magnitude than that of PbO₂ 0.25 x10³- 1.0x10³ S.cm), [30], [31] the higher conductivity favors to electron transfer. When the deposition potential is 1.55V, the diffraction peak intensity of PbF₂ in figure 4S_{1.55V} is strongest, which is consistent with results in table 1; when the potential is lower than 1.55V, because of the low electric field intensity, the migration rate of F⁻ drop, so amount of F⁻ doping in the electrode reduces; when the potential is higher than 1.55V, although the migration rate of F⁻ speeds up, but the solubility does not change; however, the enhancement of the anode oxidation potential will greatly speed up electro-oxidation reaction of Pb⁺², the change consequentially leads to the certain decrease of F⁻ doping content in the electrode.

In short electrochemical oxidation from Pb⁺² to Pb⁺⁴ occurs simultaneously with chemical deposition of PbF₂ throughout the preparation process. When the potential is low, the produce rate of PbO₂ is low; thereby, the relative content of PbF₂ deposited into the electrode increase; when the potential is high to certain value, the production rate of PbO₂ is fast, the relative content of PbF₂ decreases.

C. Effect of F⁻ doping on the surface morphology

Figure 5 shows the SEM micrographs of the F-PbO₂ electrode with different doping content of F⁻ (a-d) and the free doping PbO₂ electrode (e), to compare figures 5(e) with figures 5(a-d), it is found the many irregular columnar crystals present on the electrode surface, as PbO₂ crystal follow a three dimensional growth mode in the electrodeposition process. The

crystal on the surface of (a-d) samples tend to uniformity planarization, indicating that the F^- doping significantly change the surface morphology of the electrode and play the role of inhibiting vertical growth of PbO_2 crystal. At the same time, the crystal grain in the F^- doping on the surface of PbO_2 become fine, and the grains size drop to different extent ,

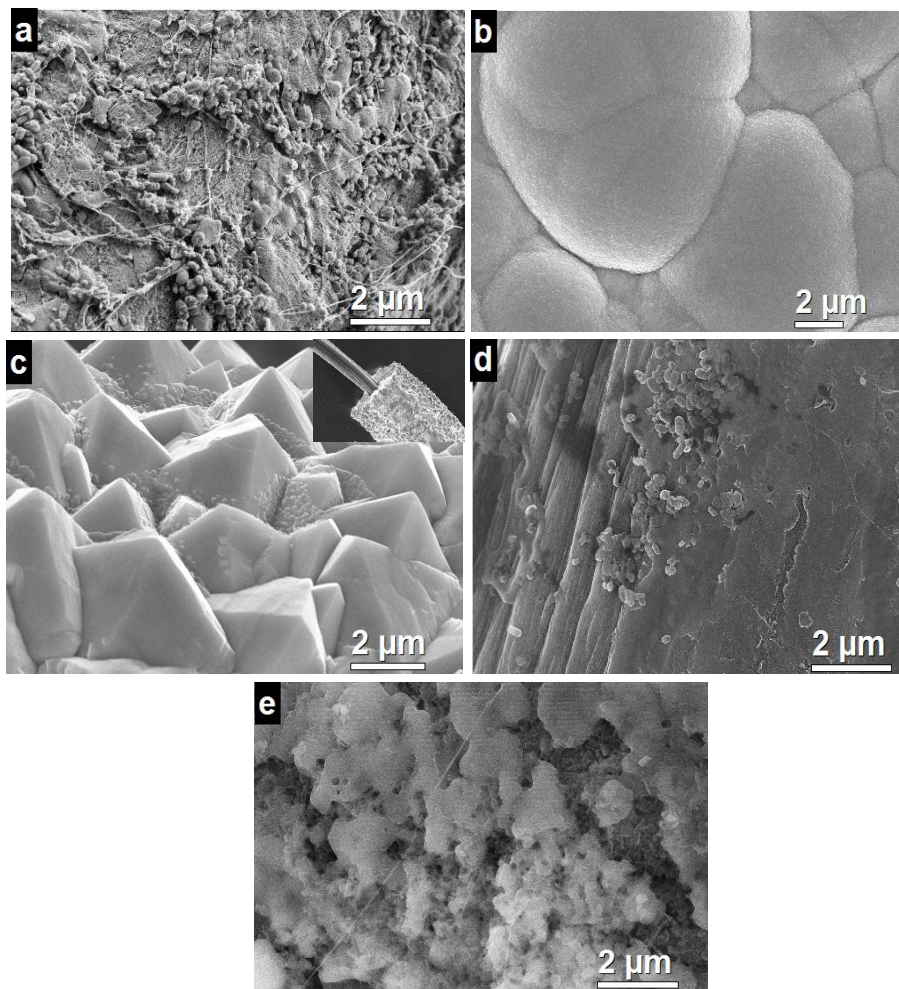


Fig.5 SEM micrographs of the F- PbO_2 electrodes with different doping potential and content of F (Atomic ratio of F to Pb are (a):0.23:1.5,b:0.86:1.2,c:0.15:4.5,d:0.09:0.9 and e the free doped PbO_2 electrode).

which could be interpreted that F^- adsorbed on the electrode surface takes part in PbO_2 crystal growth and destroys the original growth trend of the PbO_2 crystal. These two crystals grow simultaneously and complete with each other. The energies of different crystals faces are discriminatory. When the energy is high, the crystal will grow along this crystal face. However, F^- occupies the position with higher energy more easily than hydroxyl radical OH^- , due to its radius is small. Therefore, the growth of the PbO_2 crystals is blocked at active sites and would select the sites slightly lower energy, the growth of PbO_2 crystal grain is limited, the chance of crystal nucleus growth increase. Therefore, the electrode surfaces become uniform and smooth. The morphologies of the F- PbO_2

electrode and the free doping PbO_2 electrode show significant difference at 1.55V, as shown in figure 5(c) compare to 5(e).

The effect of the deposition potential on the morphology is obvious; the F^- doping content is an important factor for change of the surface morphology. When the deposition potential is low, the F content in the electrode is relatively high; the crystallites are spherical as shown in figure 5(a) $S_{1.45V}$ aggregate into many large grains, whereas, spherical crystallites in figure 5(b) $S_{1.5V}$, separately exist and clear octahedral in figure 5(c) $S_{1.55V}$ which meet the proper setup micrograph of F- PbO_2 doped. When the potential deposition is high the F content in the electrode is relatively low, and the electrode surface shown intense smaller aggregate in figure 5(d) $S_{1.6V}$. Reasonable explanation is that the more positives potential would

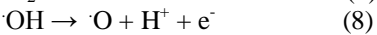
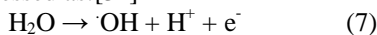
speed up the rate of electrochemical reaction of foaming PbO₂ on the surface; definitely, the vertical growth rate increase, the plane growth rate decrease, so porous surface with many smaller aggregate is formed.

D. Effect of F⁻ doping on the electrochemical properties

Fig 6 shows the linear sweep voltammetry of the F-doping electrode with different doping content of F and the free one

samples (S_{1.45V}, S_{1.5V}, S_{1.55V}, S_{1.6V}, S_{free1.55V}), doped PbO₂ electrode condition temperature 70 °C in 0.5mol/L Na₂SO₄ for one hour.

From the comparison of the curves (S_{1.55V}) and others, it can be seen clearly that the effect of the F-doping on the oxygen evolution potential is significant, the minimum decrease value of initial potential for oxygen evolution is shown on sample (S_{1.55V}) corresponding electrode that prepared at 1.55V, meet the atomic ratio of Pb to F is 4.5: 0.15, and namely, the Pb doping content also is the highest and F doping content also is the optimized. Comparing with the free- doped PbO₂ electrode, the oxygen evolution reaction at the anode is restrained, because the F-doping it related with amount of F-doping. The change trend of the curves in the figure 6 is consistent with XPS results, indicating that the electrocatalytic activity of the electrode can be change through regulating the deposition potential to control the F-doping content. The fact about the effect of F-doping on oxygen evolution process has been observed at the PbO₂ electrode. The electrochemical properties of the PbO₂ electrode can be improved by controlling the content of F- doping in order to meet the requirement of some specific of electrocatalytic reaction. For example, the formation of the hydroxyl radical ·OH can be controlled by inhibiting and promoting the discharge process of H₂O on the electrode surface. In the acidic solution, oxygen evolution reaction can be expressed as:[32]



PbF₂ produced by Pb⁺² and F⁻ can affect the growth of PbO₂ on the crystal face with highest energy. It was confirmed that the higher content of PbF₂ can make the surface morphology of the electrode become more uniform, the surface state favor to the improvement of the electrode properties. However, the existences of F⁻ increase the steric hindrance of ·OH adsorption on the electrode surface.

That is, the formation of F- will reduce active sites of oxygen evolution on PbO₂ electrode. It can be known from the reactions (7),(8) and (9) that the decrease of adsorbed ·OH would slow down the rate of oxygen evolution, thereby, the F- PbO₂ electrode displays the highest potential of oxygen evolution. As we all know, the increase of oxygen evolution potential can accelerate chlorate oxidation, so then improve the

production efficiency under certain conditions. Because the oxygen evolution reaction and oxidation reaction of the developing sodium perchlorate is pair of competitive reaction, the anode with high overpotential of oxygen evolution can enhance current efficiency of oxidizing chlorates and decrease the consumption of the electric energy, this very significant for the chlorates oxidation, waste water treatment and environment protection.[33]

electrochemical performance has been characterized for the suggested electrode by Electrode stability Figure 7a, compares the stability of the F-PbO₂ doped with free doped electrodes by accelerated life tests. As seen in Figure 7, the PbO₂ electrode had a service life of time work, which was 37 times longer than that of the free doped electrode. This is attributed to the different morphologies of F-PbO₂ doped and free doped electrodes. Cyclic voltammetry (CV) Fig.7b shows CV at positive and negative redox area of the F-PbO₂ electrodes (S_{1.55V}) using electrolyte(1MKCl +5mM K₃Fe(CN)₆) at room temperature, scan rate 5mV·s⁻¹ voltammograms fig 7 b results confirmed the influence of the chlorate by oxidation, tested CV with chlorate where a passivation film was formed on the surface of the PbO₂ electrode during the oxidation, which prevented all reactions further occurring on the surface of the electrode, and without sodium chlorate, enlarge peak of oxidation appeared. The electron-transfer kinetics and the reversibility of the electrode reaction of the excluded chlorate condition, showed electrode performance superior to the mixed electrolyte in CV measurements.[34],[35]

Figure 7 c, results of bulk electrolysis was showed the productionability can be readily change of chemically oxidation of sodium chlorate electrolyte concentration 100g/l with charge passed during sodium chlorates electrolysis, anode S_{1.55V} F-PbO₂ doped electrode, optimized condition of different voltages of conversion (S_{3V},S_{3.5} and S_{4V}), cell body volume 100ml, temperature and PH are adjusted to 55°C and 6.5 relatively, the graph showed S_{4V} have good working electrode at 4V adjusting, with efficiency 83.6%, it is expected that, this S_{1.55V} F-PbO₂ electrode could be extensively applied in industries.

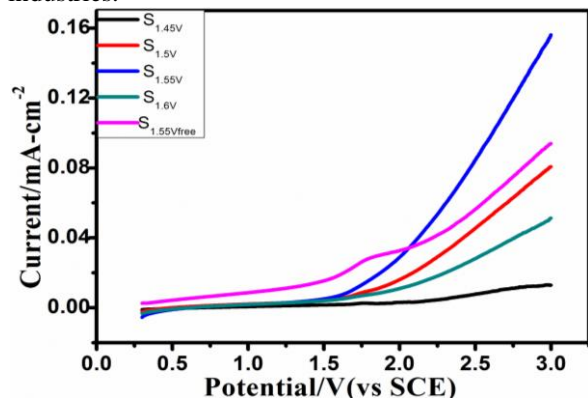


Fig 6. a Linear Sweep Voltammetry of the F-PbO₂ electrode with the different doping content of F and the free doped PbO₂

electrode, scanning rate 5mVs^{-1} , $0.5\text{MNa}_2\text{SO}_4$ as electrolyte against SCE electrode; electrolytic cell with fourth electrodes.

Fig.7 d shows current and efficiency changes within the electrolytic Cell. This one of the basic requirements for materials acting as an efficient electrode can be described as high chemical stability, large specific surface area, good fluid permeability, high electrical conductivity and structural continuity, cheap and easily available.

This can theoretically guarantee an operation under a more efficient and desirable diffusive control mode. Moreover, it will be more desirable for this material to operate under more elevated electrical conductivity conditions, in which can be reached through an adequate reactor design that accept the material.

A decreasing of current efficiency with increasing of current intensity would normally be expected due to the production come out. Electrolysis is a process by which electrons are forced through a chemical cell, thus causing a chemical reaction. The positive charge usually attracts electrons, and the electrode providing electrons is called cathode, because reduction takes place on it. Species with negative charge oxidized on the anode, many reactions will occur, impurities hinder the mobility of current and lowered the efficiency.

The maximum current efficiency obtained in this investigation was 83.6%, has lower current density 25Ma . The cell is of simple geometric easy to design.

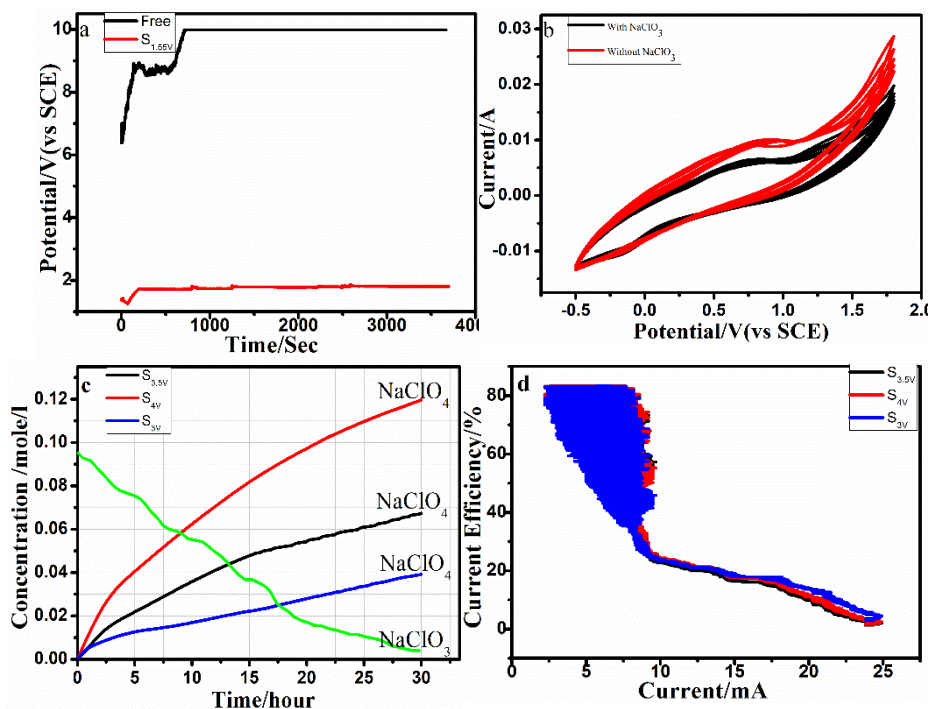


Fig 7: a shows optimized electrode $S_{1.55V}$ stability. Test of electrode potential (vs SCE, fourth electrode Cell in $2\text{MH}_2\text{SO}_4$, current 1Acm^{-2} , temperature 70°C for one hour) compared in detail for the electrochemical oxidation process with free doped electrode; b Cyclic voltammograms of $S_{1.55V}$ in $(1\text{MKCl} + 5\text{mM K}_3\text{Fe}(\text{CN})_6)$ with and without 500mg/l ClO_3^- , scan rate 5mVs^{-1} ; c shows ClO_4^- and ClO_3^- Concentration as a function of time, at different potential of electrode $S_{1.55V}$, 100g/l NaClO_3 , $\text{PH}=6.5$, Temperature 55°C , time 30hour; d show current and efficiency change within the Cell.

IV. CONCLUSIONS

The influence of both element graphite substrate and fluorine to F-doping PbO_2 electrodes was obtained by potentiostatic deposition at anode. The content of F-doping in the electrode had been controlled by adjusting the potential in the electrodeposition process. The electrochemical oxidation of sodium chlorate to perchlorate can be proceed efficiently when set suggested electrode $S_{1.55V}$, set potential much to S_{4V} , then electrolyzed using cathode of Ru/TiO_2 with a temperature of 55°C . The larger the F content is, the smaller the crystallite size is, the octahedral F-doping can make the electrode surface become larger and

active. The content of F play role as catalyst of easy oxygen evolution potential. Therefore, the application range of the PbO_2 electrode become wider.

ACKNOWLEDGEMENTS

This study was financed from Marble Engineering Company through University Research, and Experimental work was supported by Beijing University of Chemical Technology (BUCT China), I gratefully appreciated prof. Wan Peingu, and his team of electrochemical department, my acknowledged extend to thanks whom on the way reflected fruitful efforts.

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