



Rapid Removal of the Passivation on Iron Anode Surface by Oxalic Acid for Ferrate(VI) Generation

H.J. ZHANG

School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, P.R. China

Corresponding author: Tel/Fax: +86 27 62013553; E-mail: sallyqing_zhj@163.com

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A convenient anodic pretreatment was established based on the possibility of dissolution of passivation using oxalic acid. Then, X-ray photoelectron spectroscopy and scanning electron microscopy examinations were used to examine the composition and structure of anode surface, respectively. The high removal efficiency of passivation and the formation of porous structure on anode surface could be observed. These led to significant enhancement of the ferrate(VI) synthesis efficiency. The characteristics of ferrate(VI) solution such as stability and reproducibility were studied by flow-injection chemiluminescence method based on the chemiluminescence reaction of ferrate(VI)-luminol. The chemiluminescence signal was stable for a week. The relative standard deviation (RSD) was 2.41% for five runs of electrolysis.

Key Words: Oxalic acid, Anodic pretreatment, Ferrate(VI), Flow-injection chemiluminescence analysis.

INTRODUCTION

Hexavalent iron species [ferrate(VI)] have been known due to its strong oxidizing properties, relatively high redox potential and environment-friendly reduction product. This is quite interesting in a pure scientific curiosity and also in its possible applications such as the treatment of contaminants and toxins in water and wastewater^{1,2}, clean technology for organic synthesis^{3,4}, high energy density rechargeable batteries^{5,6}, but rarely paid attention on its potential use for analytical chemistry.

The preparation methods of ferrate(VI) includes thermal, chemical and electrochemical techniques. The electrochemical method has been chosen as the most suitable method for ferrate(VI) generation, because of its simplicity, reduced costs (no chemical oxidant is required). However, the application of electrochemical method is limited by low synthesis rate, instability of ferrate(VI) solution and poor electrolytic reproducibility. A key factor is the formation of passivation. First, this passivation process forms a firm oxide film on anode surface, which leads to a low current efficiency. It can cause a gradual decrease of synthesis rate and a poor reproducibility of electrolysis⁷. In addition, Fe(III) ions dissolved from passivation layer can accelerate a decomposition of ferrate(VI) and lead to a instability of ferrate(VI) solution⁸. The anode is traditionally cathodic polarized by applying a current density of 20 mA/cm² for 0.5 h in 14 mol/L NaOH solution to effectively destroy the passivation before electrolysis⁹. Obviously, this procedure

is time-consuming and unsuitable for ferrate(VI) applications, especially for analytical chemistry. In addition, it is costly owing to consumption of a large amount of NaOH. Herein, we tested the possibility of rapid removal of the passivation using oxalic acid for ferrate(VI) generation. The composition and structure of anode surface were analyzed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. Furthermore, based on the homogeneous chemiluminescence reaction of ferrate(VI)-luminol¹⁰, the stability and the reproducibility of electrochemically-prepared ferrate(VI) were studied by a flow-injection chemiluminescence (FI-CL) system. The stable and reproducible chemiluminescence signal indicated that ferrate(VI) had a great application potential in analytical chemistry.

EXPERIMENTAL

All reagents used were of commercially available and analytical grade. Oxalic acid and NaOH were from Sinopharm Chemical Reagent Company Limited (Shanghai, China). All the solutions were prepared with doubly distilled water.

The structure of the anode samples were examined by XPS analysis using a XSAM800 electron spectrometer (KRATOS Company, Britain). A monochromatic MgK α X-ray source (1253.6 eV) was operated at 12.5 kV, 16 mA for all anode samples, along with pressures in the analysis chamber of more than 6×10^{-7} Pa; the measurement area was 10 mm \times 6 mm. The binding energy was calibrated by assigning the C (1 s) peak to 285.0 eV. The relative amounts of different

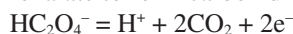
elements, within the probe depth of the technique (5-10 nm), were estimated from component peak areas after background subtraction and sensitivity factor correction. The morphology of the anode samples was obtained using SEM with a quanta 200 microscopy (FEI Company, Holland).

A divided two-compartment laboratory electrolyser described elsewhere was used to prepare the ferrate(VI) solutions¹⁰. The flow-injection chemiluminescence detection system was homemade and similar to that described in the previous literature¹⁰. The pretreatment procedure was as follows: the iron anode was washed with distilled water, treated in 0.05 mol/L oxalic acid solution for 5.0 min duration, sonicated in distilled water within 30.0 s duration and rinsed with distilled water again to remove the residual oxalic acid on the electrode surface. The concentration of ferrate(VI) in the anolyte was measured by the chromite method¹¹.

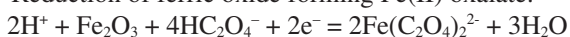
RESULTS AND DISCUSSION

The passivation on the anode surface could be dissolved and removed by oxalic acid via a reductive mechanism. The overall reaction was a redox reaction, formed by two half cells:

Oxidation of oxalate to form carbon dioxide:



Reduction of ferric oxide forming Fe(II) oxalate:



The overall reaction is therefore:



Accordingly, the effect of pretreatment of iron anode by oxalic acid for ferrate(VI) generation was probed from 0-20.0 min. The best yield reached and stabilized at 5.0 min duration. And this was chosen as the best condition for the following experiments. Compared to that obtained by cathodic polarization⁹, the yield was improved and increased nearly 30 %. More importantly, the pretreatment duration was greatly shortened by this developed method.

Fig. 1 presents the XPS survey spectra for the anode treated by the proposed method and the traditional method, respectively. The lower contents of Fe_2O_3 of the anode surface demonstrated that this proposed method was more benefit for the passivation removal. In addition, the appearance of anode surface treated by the developed method was also examined by SEM (Fig. 2). The porous surface was observed obviously. The results obtained above were evident that ferrate(VI) yield was significantly enhanced due to the high removal efficiency of passivation and the porous structure on the anode surface, which were consistent with the conclusions reported in the literatures^{9,12}.

The stability of electrochemical synthesis ferrate(VI) in 14.0 mol/L NaOH solution were traced by flow-injection chemiluminescence method. To study the effect of storage temperature on stability, chemiluminescence intensities were examined at temperatures of 1, 20 and 50 °C. The results in Fig. 3 show that the chemiluminescence intensities had decreased 14 and 30 % by the end of the 75.0 min at 20 and 50 °C, respectively. At a temperature of 1 °C, the chemiluminescence signal was stable for nearly a week. It showed that increased storage temperature cannot be utilized in practice due to the very limited stability of the solution at high temperature.

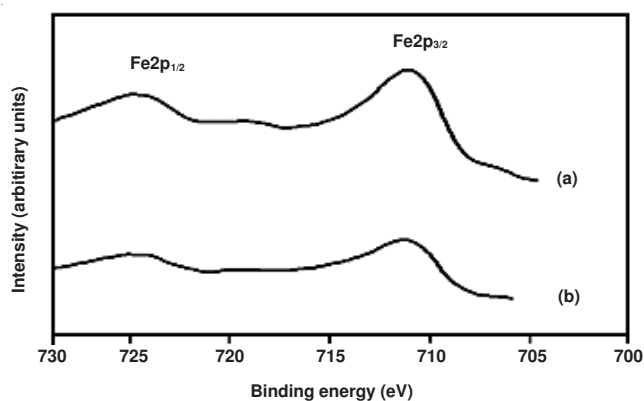


Fig. 1. Core level Fe2p spectrum for the iron anode using different treatment methods. (a) the treatment method was the same as reported [Ref. 9]; (b) the iron plate was washed with distilled water, treated in 0.05 mol/L oxalic acid solution for 5.0 min duration, sonicated in distilled water within 30.0 s duration and rinsed with distilled water

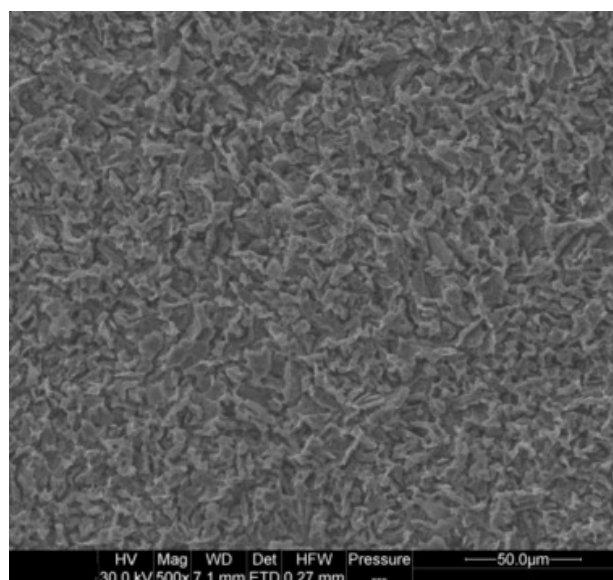


Fig. 2. SEM of the surface of iron anode using oxalic acid pretreatment. The anode treatment method is the same as that in Fig. 1b

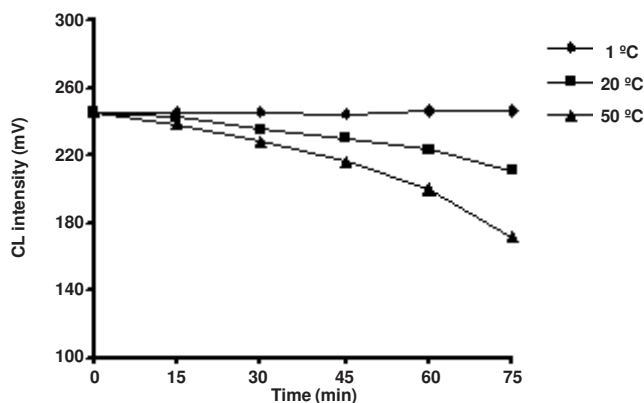


Fig. 3. Stability of ferrate(VI) solution at different storage temperature. Electrolysis current, 1.0 A; electrolyte, 14.0 mol/L NaOH; electrolysis duration, 20 min. The anode treatment method is the same as that in Fig. 1b

The reproducibility of electrochemical synthesis of ferrate(VI) solution was demonstrated. Compared with the five runs of electrolysis, the relative standard deviation (RSD) of the peak height was 2.41%. The repeated signals indicated the electrochemical-prepared ferrate(VI) solution with good reproducibility was suitable for its analytical applications.

Conclusion

The feasibility of anodic pretreatment using oxalic acid was demonstrated in this study. Because of its acid strength, good complexing characteristics, high reducing power and low risk of contamination, oxalic acid was found to be the most promising for anodic activation. This developed pretreatment has many advantages, such as short treating time, simple operation, good reproducibility, high ferrate(VI) synthesis efficiency and so on. It would be adopted as an alternative pretreatment method in the further study of electrochemical-prepared ferrate(VI) solution. The stability and the reproducibility of ferrate(VI) solution by using this developed pretreatment at low storage temperature were good enough to be directly used for analytical chemistry.

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Contact:

Ms. Ashley Han, BIT LCES-2011 Organizing Committee, 26 Gaoneng St., R401,

Dalian Hightech Zone, Dalian, LN 116025, China.

Tel:+0086-411-84799609(ext.821), Fax:+0086-411-84799629,

E-mail:ashley@lcesummit.com, <http://www.lcesummit.com/index.asp>