

전기화학적 매개 산화공정에서 전해셀의 성능 평가

정상준, T. Ramesh, Vladimir Bobrov, 문일식*
 순천대학교 공과대학 화학공학과
 (ismoon@sunchon.ac.kr*)

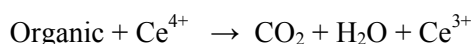
Performance Estimation of Electrochemical Cell in the Medicated Electrochemical Oxidation Process

S. J. Chung, T. Ramesh, Vladimir Bobrov, I. S. Moon*
 Department of Chemical Engineering, Sunchon National University, Sunchon, Korea
 (ismoon@sunchon.ac.kr*)

Introduction

Relatively large quantity of organic liquid wastes containing complex and non-degradable agents is generated from the chemical decontamination companies. With increasing the utility of chemical decontamination, safe and effective treatment for waste reduction and final disposal is required. Some of the commonly applied conventional treatments for the disposal of non-degradable organic wastes include incineration, landfill and biological treatment[1]. The incineration of organic waste poses emission problems such as discharge of very toxic materials in the off-gas in the case of improper combustion.[2]

Electrochemical oxidation of hazardous organics wastes is a promising alternative and an emerging technology, which allows complete mineralization of organic materials at modest temperature. Organic wastes are destroyed by Mediated Electrochemical Oxidation process which oxidizes combustible organic waste at low temperature and atmospheric pressure [3]. The MEO technique offers several advantages which are inherently safe system. This process is non thermal that is it does not as thermal energy to break down and destroy organic waste [2-6]. The mediators as strong oxidant allow oxidizing the organic waste completely converted into carbon dioxide and water.



The mediator is a multivalent metal ion which cleanly recycled in the process [4]. The most commonly used mediator are silver, cobalt, iron and cerium with various acids.

In the MEO process, the electrochemical cell is an important component of the operation. The electrochemical cell consists of an anode and cathode separated by a membrane. In the electrochemical cell, oxidation of Ce(III) to Ce(IV) in electrolyte occurs at the anode. Therefore, degradation of organics depends on performance of electrochemical cell. And corresponding reduction of nitric acid to nitrous acid will occur at the cathode, then recovery of nitric acid by the oxidation of NO and capture in water.

This study was performed with the aim of evaluating the performance of electrochemical cell, which comprised different types of electrode and then assembled in series. The degradation of phenol in MEO process was also investigated.

Experiments

In this experiment, the electrochemical cell consisted of anode and cathode of dimensions 9.7×14.5×0.5 cm, which separated by selective fluoropolymer membrane. Two types of electrode were used in this study, plate electrode having the dimensions of width 14 cm and length 20 cm and mesh

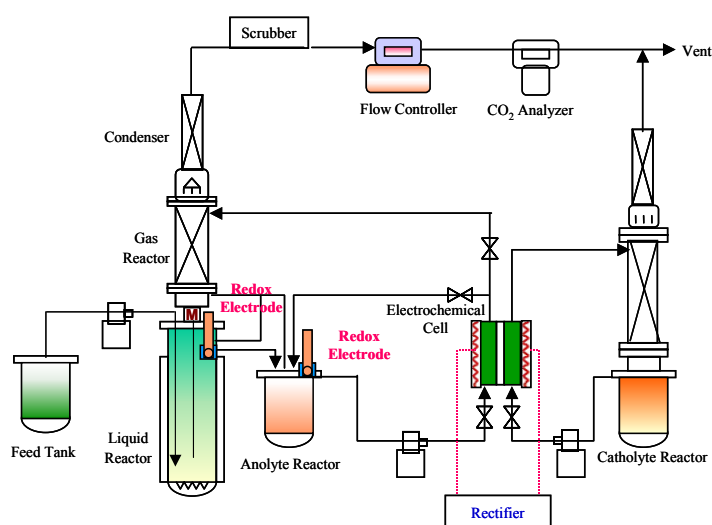


Fig. 1. Schematic diagram of the experimental apparatus.

electrode having the dimensions of width 9.5 cm and length 13.7 cm. One electrochemical cell comprised plate electrode which made of platinum, other electrochemical cell comprised platinum mesh electrode which was coated with iridium.

The electrochemical cells are assembled in series. In case of series 1, each electrochemical cell to be electrically connected through terminals of anode and cathode. In series 2, the electrode in the interior of the electrochemical cell is bipolar and supports the cathode reaction on one side and the anode reaction on other side.

The anolyte solution consisted of 1M $\text{Ce}(\text{NO}_3)_3$ and 3M HNO_3 mixture. 4M HNO_3 as the catholyte used in this study. The temperature of the anolyte and the catholyte solution was maintained constantly by heating mantles. Air was continuously sent into the catholyte solution to convert nitrous acid to nitric acid during this reaction.

In order to measure concentration of Ce(IV), redox potential of anolyte solution was measured by pH/ISE meter(Orion Co. Ltd., Model 720A) using Pt-Ag/AgCl combined electrode.

During the organic destruction experiment, Phenol was injected with constant flow (10ml/min) of various concentration (1000ppm & 400ppm) in the liquid phase reactor after the redox potential of anolyte reached to the maximum value. In the process, nitrogen supplied to carries the carbon dioxide gas and concentration of carbon dioxide was measured using the CO_2 analyzer(Environmental Instruments, Anagas CD 98). A schematic of the MEO process is shown in Fig. 1.

Results and Discussion

Fig. 2 and 3 shows that the performance of electrochemical cell for plate electrodes with mesh electrodes. In case of mesh electrodes, current increased with supply voltage that mesh electrodes were 2 times than plate electrodes and the conversion ratio of Ce(III) to Ce(IV) increased with the reaction time in the mesh electrodes as compare to plate electrodes. Therefore, we can expect that energy consumption for Ce(III) oxidation of mesh electrode type cell will be decreased than with plate electrode at the optimum current.

From above results, the mesh electrodes type electrochemical cell is more efficient in the mediated electrochemical oxidation.

Fig. 4 and 5 shows that the performance of electrochemical cell for series 1 and series 2. The current increased with supply voltage that series 1 was more 1.5 times than series 2 and

the conversion ratio of Ce(III) to Ce(IV) was increased with the reaction time in the series 1 as compare to series 2.

The conversion rate of Ce(III) to Ce(IV) of the series 1, was higher than the series 2, at 6V. In spite of high current for the series 1, consumed energy for Ce(III) oxidation was found to be higher compared to the series 2. This is because the excess current supplied on series 1 is consumed for the hydrolysis reaction in electrolyte. The energy consumption for Ce(III) oxidation of the series 1 when optimum current supplied, must be decreased than the series 2. Further experiments are underway to examine the performance of the series cells.

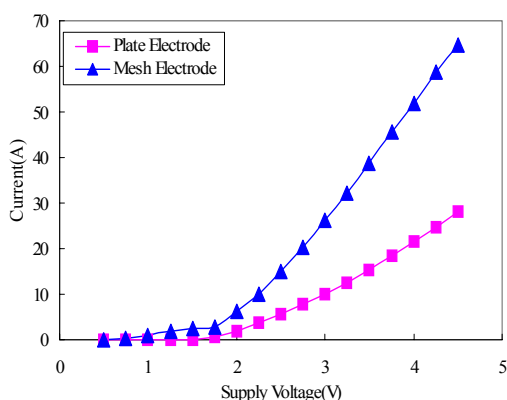


Fig. 2. Voltage-current characteristic for plate electrodes and mesh electrodes in the electrochemical cell at zero time (1M Ce(III), 3M HNO₃).

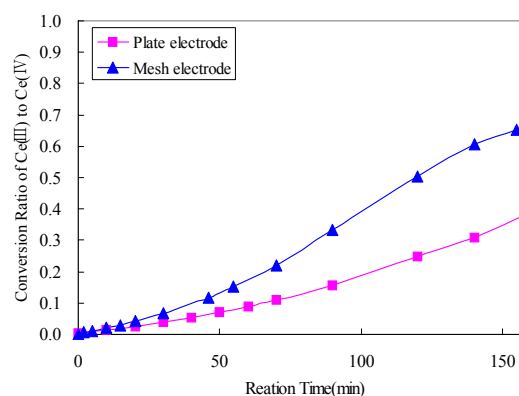


Fig. 3. Conversion ratio of Ce(III) to Ce(IV) with reaction time for plate electrodes and mesh electrodes in the electrochemical cell at 3V, 30°C (1M Ce(III), 3M HNO₃).

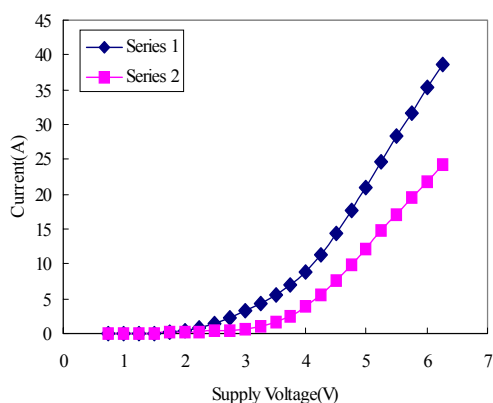


Fig. 4. Voltage-current characteristic for series 1 and series 2 at zero time (1M Ce(III), 3M HNO₃).

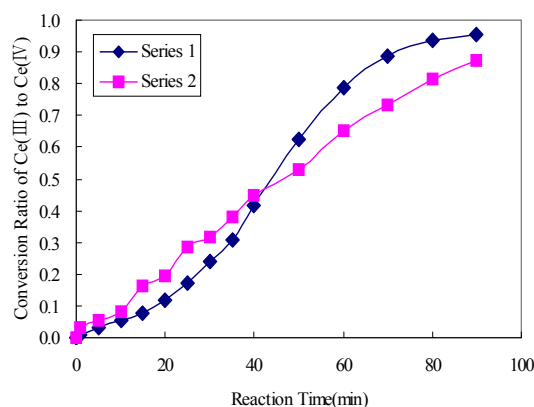


Fig. 5. Conversion ratio of Ce(III) to Ce(IV) with reaction time for plate electrodes and mesh electrodes in the electrochemical cell at 6V, 80°C (1M Ce(III), 3M HNO₃).

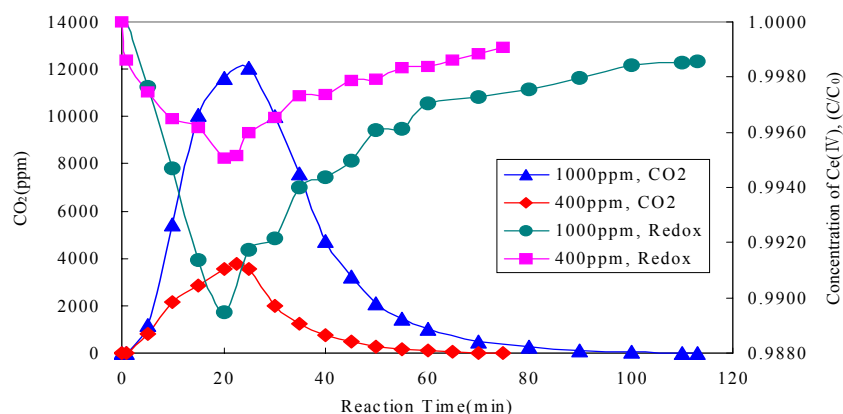


Fig. 6. The relation of evolution of CO₂ and concentration of Ce(IV) in phenol degradation by Ce(IV) at 80°C

The degradation of phenol in MEO process using series cell is shown in Fig. 6. 20 min was required for complete injection of phenol solution. Concentration of Ce(IV) was decreased till injection of phenol solution finished, and concentration of Ce(IV) was increased after injection of phenol solution. The quantity of evolved CO₂ was increased with increase in quantity of phenol in Ce(IV) solution. Based on our results it was evident that Ce(IV) was efficient in phenol degradation. The works of optimization on phenol degradation in MEO process need to conduct in the future.

Acknowledgements

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References

1. Y.H. Chung, and S.M. Park, "Destruction of aniline by mediated electrochemical oxidation with Ce(IV) and Co(III) as mediators", *J. Appl. Electrochem.* 30, 685-691(2000).
2. D.F. Steele, D. Richardson, J.D. Campbell, D.R. Craig and J.D. Quinn, "The Low temperature Destruction of Organic waste by Electrochemical Oxidation", *Trans IChemE*, Vol 68, part B,115-121(1990).
3. Martyn G. Adamson, Zoher Chiba, Erica H. von Holtz and Ronald D. Streit, "Development of Advanced Waste Treatment Technologies for Demonstration in the Mixed Waste Management Facility", presented at the Third Biennial Mixed Waste Symposium, Baltimore, MD August 7-11(1995).
4. Norvell Nelson. "Electrochemical Destruction of Organic Hazardous Wastes. The Cerium oxidation CerOx Process Electrochemical Cell," *Platinum Metals Rev.*, 46, (1), 13-23(2002).
5. Joseph C. Farmer, Francis T. Wang, Ruth A. Hawly-Fedder, Patricia R. Lewis, Leslie J. Summer and Linde Foiles, "Electrochemical Treatment of Mixed and Hazardous wastes: Oxidation of Ethylene glycol and Benzene by Silver(II)", *J. Electrochem. Soc.*, Vol139, No.3(1992).
6. Zoher Chiba, Bruce Schumacher, Patricia Lewis and Laura Murguia, "Mediated Electrochemical Oxidation as an Alternative to incineration for mixed waste", presented at the W.M. 95 Symposia, Tucson, Arizona, (March 1, 1995).