

Continuous MEO Process: Study on Electrochemical Cell Characteristics and Model Fitting to Organic Oxidation

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Introduction

Mediated Electrochemical Oxidation (MEO) which has been identified as one of the promising technologies by the United Nations environmental program for use in the developing countries is a promising innovative technology for the destruction or decontamination of persistent organic pollutants [1].

The electrochemical cell is a core component in the MEO technology. The previous works on MEO employed as commercial cells from different manufacturers and home-made, but details were not available.

In this paper, we describe the performance of home-made electrochemical cells with plate and mesh electrodes for Ce(IV) regeneration. The model is proposed to calculate a cerium(IV) current consumption in organic destruction MEO process and a number of “standard” cells for maintaining cerium(III)/cerium(IV) ratio at the same level. The model is based on a limiting anodic current approach corrected by oxygen evolution current and previously derived by us continuous mode organic destruction model.

Experimental

The schematic diagram of the MEO system used for this study is shown in Fig 1. The system consists of an anolyte, catholyte, and chemical reactors with the capacity of 1.5 L, respectively. The anolyte and catholyte solutions were circulated through the cell with a ceramic pump. The mediator solution oxidized at the cell was transported to the chemical reactor equipped with a scrubber and an online CO₂ analyzer. The organic solution was fed to the chemical reactor from the feed tank. The catholyte part was also provided with a gas scrubber to capture the nitrous vapors produced.

The anolyte solution was prepared by dissolving 1M cerium(III) nitrate in 3M nitric acid. The catholyte was a 4M nitric acid solution. Temperature was controlled by a heating mantle and air was purged continuously through a catholyte solution to convert nitrous acid, produced by reduction at the cathode, to nitric acid. The constant current was provided to the electrochemical cell by a constant DC voltage supply. During the reaction, concentration changes of Ce (IV) were monitored by measuring

the redox potential using a Pt-Ag/AgCl combined electrode with an pH/ISE meter.

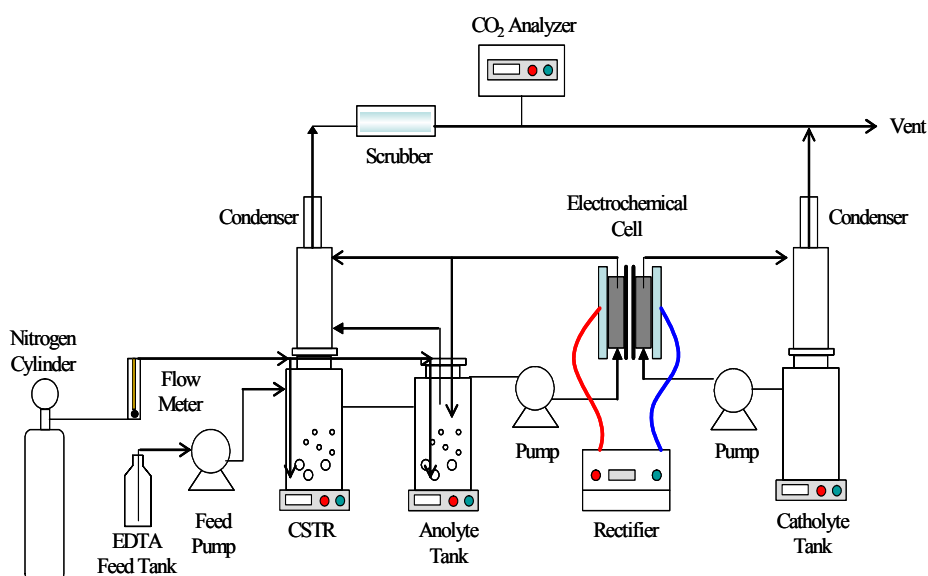


Fig. 1. Schematic diagram of the experimental setup.

Results and Discussion

In the Figure 2 volt-amperic curves are presented. They prove the applicability of limiting current approach to the cerium oxidation anodic process.

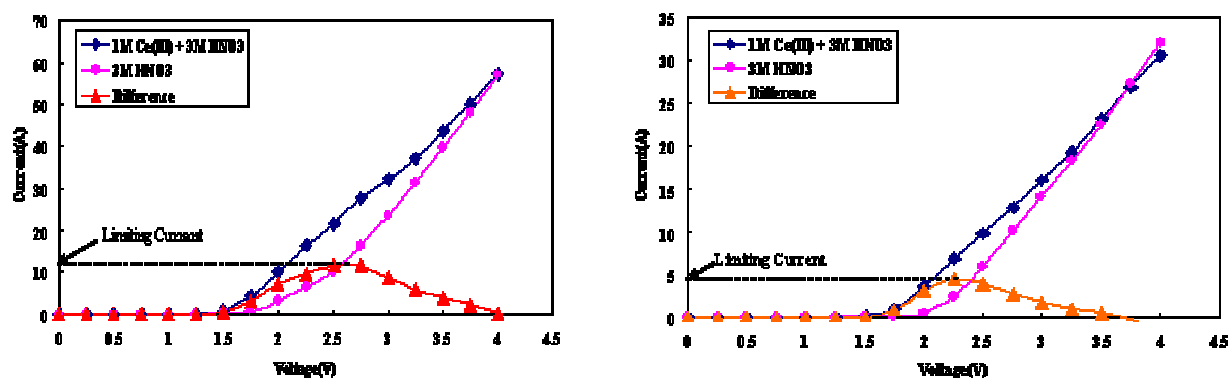


Fig. 2. Current-Voltage characteristics of MAC1 (top) and MAC2 (bottom) at 80 °C.

When cell process is applied for cerium(IV) regeneration, the rate of organic oxidation should be equal to the rate of cerium(IV) reduction. In terms of reaction and cell process characteristics, total cell current I should be equal to

$$I = n_e \nu F k C_{org} V$$

where n_e – number of electrons involved in cerium(III) oxidation, F – Faraday constant, V – MEO solution volume, ν - a stoichiometric coefficient for cerium in the reaction of organic oxidation, k - the first order rate constant of organic oxidation, C_{org} - concentrations of organic.

For EDTA taking $\nu=40$; $n_e=1$; $F=96500$ Coulomb/mole; $k=0.0007s^{-1}$; EDTA feeding rate 3ml/min and concentration 2,5%, and using “continuous process model”, current values were calculated. Results of calculations show that steady state current comes after 2 hours and is equal to 13.2 A. Our experimental results conformed by these findings.

For calculating number of cells needed for full cerium re-oxidation, mS characteristic of cell is very important. We found that this value is equal to $0.28 s^{-1}$ as for plate and mesh electrode cell. For the current 13A, it is possible to calculate the cerium(III) concentration which is suited for the process of organic destruction using limiting current approach.

The result of calculation is presented in the row N 6 of Table together with Ce(IV) concentration. The value of cerium(III) concentration corresponds to 0.48M and cerium(IV) to 0.52M. But if we want to maintain Ce(IV) e.g. at the level 0.8M we should use nearly 2.5 cells.

Table. Calculations of cerium ratio, anodic process characteristic mS and number of cells for keeping constant 13A current supply

	Ce(III), mole/dm ³	Ce(IV), mole/dm ³	$C_{Ce(III)} / C_{Ce(IV)}$	mS, cm ³ /s	No of cells
1.	0.05	0.95	0.0526	2.694	9.6
2.	0.10	0.90	0.111	1.347	4.8
3.	0.20	0.80	0.25	0.674	2.4
4.	0.30	0.70	0.429	0.449	1.6
5.	0.40	0.60	0.667	0.337	1.2
6.	0.48	0.52	0.923	0.28	1.0
7.	0.50	0.50	1.0	0.269	0.96
8.	0.60	0.40	1.5	0.224	0.8

Then these data were corrected by oxygen evolution current.

Conclusions

1. The performance of electrochemical cells of various electrode materials and geometries constructed was studied in processes of electrochemical regeneration of Ce(IV) and continuous organic destruction.
2. The new model is proposed to calculate a steady state current for organic destruction by cerium(IV) MEO process and a number of standard cells for cerium(III) re-oxidation based on a limiting anodic

- current approach and previously derived by us continuous MEO organic destruction model.
3. The rate of organic destruction process at a steady state in a continuous feeding mode and the appropriate current value is shown to be independent on its value but it is in a linear dependence of organic concentration and its flow rate.
 4. The same current cell supply keeps different cerium(III)/cerium(IV) ratios. But for required ratio, it is necessary to have appropriate cell characteristics. Additionally cerium oxidation current should be corrected by oxygen evolution.
 5. The number of standard cells applied to keep the constant conversion ratio should be optimal also from economical point.

Acknowledgements

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References

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