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Research Note

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RESEARCH NOTES

Process Parameters and Kinetics for the Electrochemical Generation of Cerium(IV) Methanesulphonate from Cerium(III) Methanesulphonate

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To study and optimize the process parameters such as current density, temperature, concentration of cerium(III) methanesulphonate and methanesulphonic acid, and kinetics for the electrochemical generation of cerium(IV) methanesulphonate in aqueous methane sulfonic acid medium. A 97% current efficiency and conversion was achieved at 5 A/dm^2 current density in 0.8 M cerium(III) methanesulphonate with 2 M methanesulphonic acid medium at 50 °C temperature.

Introduction

In the mediated electrochemical oxidation [MEO] process, an electrochemically generated metal ion is used as an oxidant. This mediator ion in acidic medium destructs virtually any organic material that comes in contact with it completely, in a totally enclosed chamber without any harmful emissions. Usually transition and inner transition metal ions such as silver, cobalt, manganese, and cerium are used as mediator ions owing to their high redox potentials. During organic synthesis/organic destruction, metal ions are reduced to their original state and again reoxidized by the electrochemical cell thus forming a closed loop.

The main advantages of the MEO process are the optimum working conditions of ambient temperature (less than 100 °C) and atmospheric pressure and regeneration and reuse of the oxidant; the products formed are only CO_2 and water, minimizing the production of secondary wastes. The oxidation of organic compounds can be brought about either by a direct electrochemical route or by an indirect route. The direct route is based on direct electron transfer from the organic substrate to the anode. The indirect route employs an intermediate inorganic redox couple. The indirect redox couple readily reacts on the electrode surface and to avoid mass transfer problems, the oxidation is brought about by a homogeneous reaction with the organic compound present in a dissolved or emulsified state.[1]

The regeneration of the redox species and the reaction with the organic compound being carried out via either an in-situ or ex-situ two-stage process. These indirect electrochemical oxidations have been supported with various inorganic redox couples like Ce(III)/(IV), Ag(I)/(II), and Co(II)/Co(III) which are used as oxidizing agents. After the reaction, the regeneration of redox couple is carried out in an electrochemical cell.[2−8] Paulenova et al.[9] and Fang et al.[10] studied the use of a cerium(III)/cerium(IV) redox system in battery and energy applications. Several processes using this mediated electrochemical oxidation have been reviewed.[11−13] Wei et al.[14] and Raju et al.[15] have recently reviewed engineering aspects of mediated electrosynthesis.

For most of the organic oxidations, the preferred acid concentration is in the range of 1.0−4.0 M methanesulphonic acid. In this region, the solubility of cerium(III) in methanesulphonic acid is about 10 times greater than the sulfuric acid. This allows much higher current density with methanesulphonic acid and lower capital cost due to less costly electrochemical and chemical reactors. Some studies were reviewed[16−19] for the use various acids like sulfuric acid and nitric acid in electrochemical generation of cerium(IV) ions.

The advantages of methanesulphonic acid over other acids are low cost, the fact that methanesulphonate is unreactive with reactants and products, stability to anodic and cerium(III) oxidations, high solubility of cerium(III) and cerium(IV), high current efficiency (>90%), fast organic oxidations, and high selectivity with many reactants.

Process investigation consists of finding kinetic parameters to get an optimum value for a given function [or optimum condition for electromediated systems]. Before estimating an optimum property, an optimization criterion has to be chosen. This may be a process variable, say, current density and concentration. On the basis of the optimization criterion, one has to develop an objective function, which relates the optimization criterion to the current efficiency, conversion and space-time yield A mathematical model may be used for the set of quantitative relationships between the important parameters. This defines the reactor characteristics and their relationships to process conditions. It is also used to discover the process conditions, variables, and other parameters.

Mediated electro-oxidation or indirect electrosynthesis is a cyclic process involving the electrochemical generation of a redox agent and use of that agent to effect a chemical reaction. A redox agent such as cerium(IV) generated in an electrochemical cell is contacted with a reactant in a conventional chemical reaction. In mediated system, the concentration of the electroactive species is the major parameter that determines the maximum feasible current density, space-time yield, and current efficiency. The amount of charge passed is normally proportional to the concentration and therefore the concentration of electroactive species will also be as high as possible.

Although several metal ions are available for use in MEO system, cerium(III) is preferred in our studies due to the following reasons: it possesses good oxidizing behavior due to its high redox potential ($E° = 1.62$ V) The rate of water oxidation is less which is an unwanted reaction and reduces the activity of mediator ion; it does not form precipitate with

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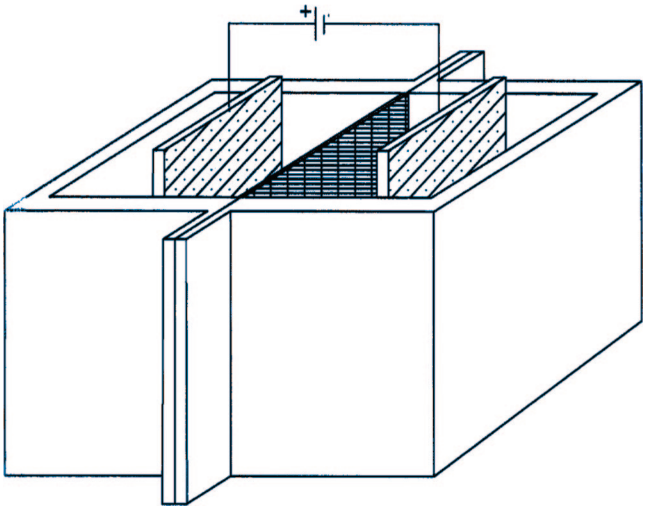

Figure 1. Schematic diagram of electrochemical cell for the Ce(III)/Ce(IV) redox system.

Table 1. Experimental Condition for Electrochemical Generation of Cerium(IV) Methanesulphonate

S no	electrochemical cell system	
1	anode	DSA-O_2 [0.4 dm^2 working area]
2	cathode	stainless steel [0.4 dm^2 working area]
3	anolyte	cerium(III) methanesulphonate in MSA
4	catholyte	1−4 M MSA
5	diaphragm	Nafion 324 membrane
6	current density	1−15 A/dm^2
7	cerium(III) methanesulphonate concentration	0.4−2.0 M
8	temperature	30−60 °C
9	anolyte and catholyte volume	175 mL
10	stirring rate	75 rpm
11	anode and cathode distance	1 cm

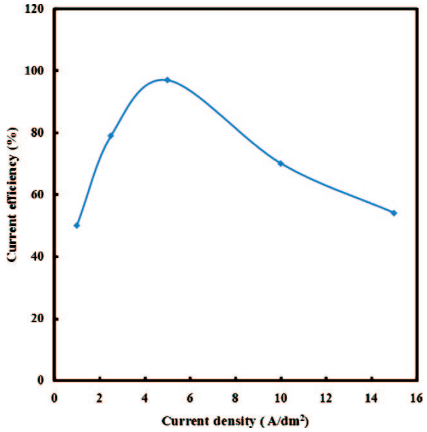

Figure 2. Current efficiency profiles for Ce(IV) generation with respect to electrolysis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, 0.8 M cerium(III), 2 M MSA, current passed = 3.8 A h, 50 °C, 75 rpm].

chlorine containing compounds; it can be recovered and reused without much loss.[20,21]

There are only a few reports/studies on the cerium(III)/cerium(IV) oxidation in methanesulphonic acid (MSA) medium. And all these studies were focused on any one of the process parameters and reaction mechanisms for electrochemical oxidation of cerium(III) methanesulphonate.

Hence, studies were carried out for the effects of current density, concentration of methanesulphonic acid, concentration of cerium(III) methanesulphonate, temperature, and rate of agitation on electrochemical oxidation of cerium(III) methanesulphonate in aqueous methanesulphonic acid medium. And kinetic study was also done for the electrochemical generation of cerium(IV) methanesulphonate.

Experimental Details

Solutions of cerium(III) methanesulphonate in methanesulphonic acid were prepared by using cerium carbonate and methanesulphonic acid and this method has been described elsewhere.[11] A batch type electrochemical cell [Figure 1] was used for the electro-oxidation of cerium(III) methanesulphonate solution.

A rectangular PVC tank cell with Nafion 324 cation exchange membrane was used for the electrochemical reaction. The anode and cathode was DSA-O_2 (mesh type) and stainless steel, respectively. Both the anolyte and catholyte chambers were maintained at 50 °C throughout the reaction. The electrolysis was carried out under constant current conditions. After the electrolysis, the anolyte solution of cerium(IV) was quantitatively analyzed by titration with ferrous ammonium sulfate using Ferrion indicator. All experimental conditions are listed in Table 1.

Results and Discussion

Studies were carried out for the electrochemical oxidation of cerium(III) methanesulphonate to cerium(IV) methanesulphonate in a divided batch cell. Anolyte and catholyte compartments were separated by a Nafion 324 cationic exchange membrane. DSA-O_2 electrode was used as the anode and stainless steel as the cathode. Constant current electrolysis was carried out to optimize the process parameters like current density, temperature, and concentration of cerium(III) methanesulphonate and methanesulphonic acid concentration. The high solubility of the cerium(III) ion in methanesulphonic acid of the concentration 0.5−4.0 M range enhances the generation of cerium(IV) ion concentration with high current efficiency (97%) at a current density of 5 A/dm^2. All the studies were carried out in a tank type batch electrochemical cell. In this cell, the anolyte was stirred by mechanical stirrer for good mass transfer.

(a) Effect of Current Density. The effects of the current density on the conversion of cerium(III) methanesulphonate to cerium(IV) methanesulphonate were investigated for the current density range of 1−15 A/dm^2. The results were shown in Figures 2 and 3. It is clear that the generation of cerium(IV) methanesulphonate is dependent on the current density. The current efficiency and conversion are increased significantly with increased current density up to 5 A/dm^2, but there was only a minor decrement in the reaction after a further increase in the current density from 5 to 15 A/dm^2.

The electrochemical generation of the cerium(IV) methanesulphonate in this reaction is highly influenced by the current density and the conversion of cerium(III) ions to cerium(IV) ions in methanesulphonic acid medium is also affected by the current density. Therefore, the current density was one of the important process parameter used to study the reaction phenomena for the generation of redox mediators. Hence, that current density affects the environment of the mediated electrochemical oxidation reaction.

(b) Effect of Current Density on Concentration of Cerium(III) and Cerium(IV). The effects of the current densities on the generation of cerium(III) methanesulphonate

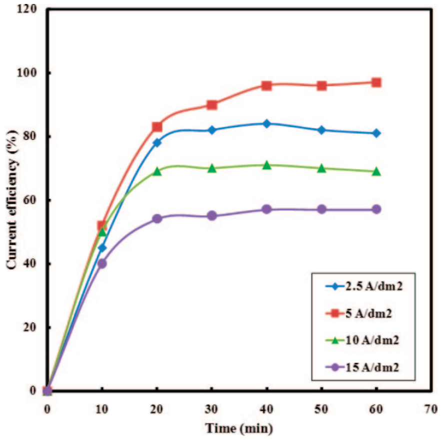

Figure 3. Current efficiency profiles for Ce(IV) generation for various current densities with respect to electrolysis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, 0.8 M cerium(III), 2 M MSA, current passed = 3.8 A h, 50 °C, 75 rpm].

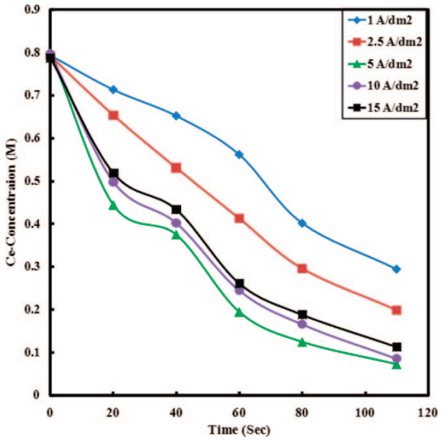

Figure 4. Concentration profiles of Ce(III) for various current densities with respect to electrolysis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, 0.8 M cerium (III), 2 M MSA, current passed = 3.8 A h, 50 °C, 75 rpm].

were studied for the maximum conversion at optimized experimental conditions. Figure 4 shows the effect of current density on the concentration of profiles ion cerium(III) ions. The conversion is relatively high with current density for the conversion of cerium(III) methanesulphonate in methanesulphonic acid medium. Some reviews reveled that methanesulphonic acid has given good conversion and good solubility for the cerium(III) ions compared other acid like sulfuric, nitric, and perchloric acid. And also, the cell voltage is low while using methanesulphonic acid as electrolyte. The concentration of cerium(III) ions decreased with increased current density. It is also found that the concentration of cerium(III) ion decreased with increase in the duration of electrolysis. This decrease is found to be more and fast at a current density of 5 A/dm^2.

Figure 5 shows the effect of current density on concentration of cerium(IV). The generation of cerium(IV)methanesulphonate is relatively high. A similar observation can be made from increased with increased current density up to a current density of 5 A/dm^2 and then decreases in all cases. It is noted that the current density affects the environment of the mediator's generation. Moreover it is found that concentration of cerium(IV) ions decreased with increased in duration at high current densities. This increase in the concentration of cerium(IV) is found to be maximum at a current density of 5 A/dm^2. With this, low reaction time is very much useful for the further use of redox mediators for other applications. For simultaneous removal of organics or other reactions using redox mediators by in situ or ex-situ reactions, this type of high conversion or generation of redox mediators is an important one.

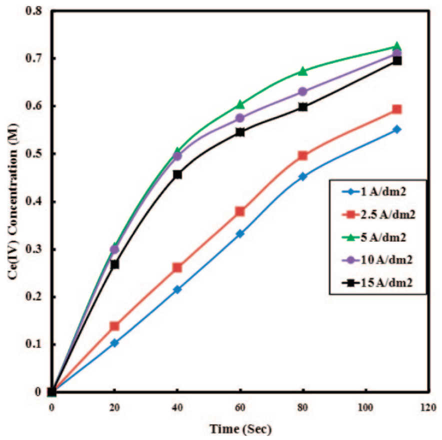

Figure 5. Concentration profiles of Ce(IV) for various current densities with respect to electrolyis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, 0.8 M cerium (III), 2 M MSA, current passed = 3.8 A h, 50 °C, 75 rpm].

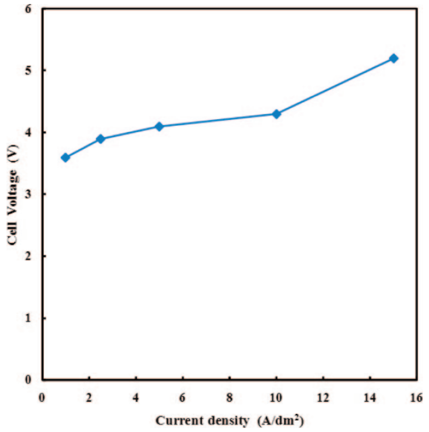

Figure 6. Cell voltage profiles for Ce(IV) generation with respect to current density [divided cell, electrodes DSA-O_2SS, volume = 75 mL, 0.8 M cerium (III), 2 M MSA, current passed = 3.8 A h, 50 °C, 75 rpm].

(c) Effect of Current Density on Cell Voltage. Figure 6 shows the variation of cell voltage under different current densities for the generation of cerium(IV) methanesulphonate in a divided cell at 50 °C. Cell voltage is an important condition for an electrochemical reaction to take place smoothly, and it is found that cell voltage increased with increased current density. The interelectrode distance was 1 cm between the anode and cathode for all the studies. The cell voltage is increased smoothly with increased current density from 3.6 to 4.1 V, and there was only a minor increment of voltage. At the end of the electrolysis the cell voltage is found to be 4.1 V at the optimum current density of 5 A/dm^2.

(d) Effect of Temperature on Current Efficiency. The effects of the temperature on the mediated electrochemical oxidation of cerium(III) methanesulphonate were investigated for the temperatures of 30−60 °C in an divided batch cell. The electrolysis was carried out at an optimum current density and the influence of temperature on conversion of cerium(III) methanesulphonate to cerium(IV) methanesulphonate were studied. The results are shown in Figure 7, and it is clear that the generation of cerium(IV) ions increased with increased temperature and the current efficiency increased from 50% at

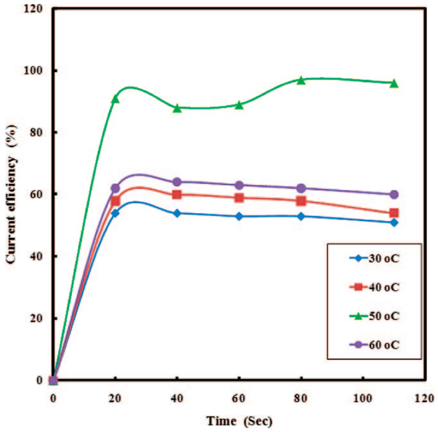

Figure 7. Current efficiency profiles for Ce(IV) generation at various temperature with respect to electrolysis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, 0.8 M cerium(III), $d = 5$ A/dm^2, 2 M MSA, current 75 rpm].

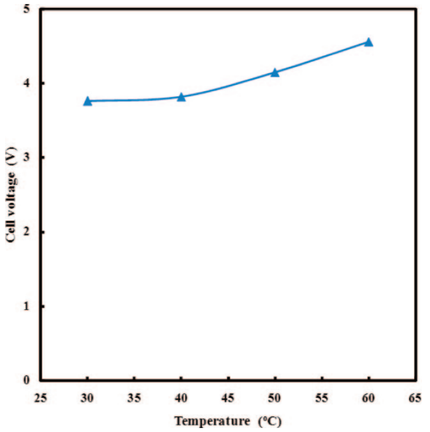

Figure 8. Cell voltage profiels for Ce(IV) generation with respecct to temperature [divided cell, electrodes DSA-O_2SS, volume = 75 mL, $d = 5$ A/dm^2, 0.8 M cerium (III), 2 M MSA, 75 rpm].

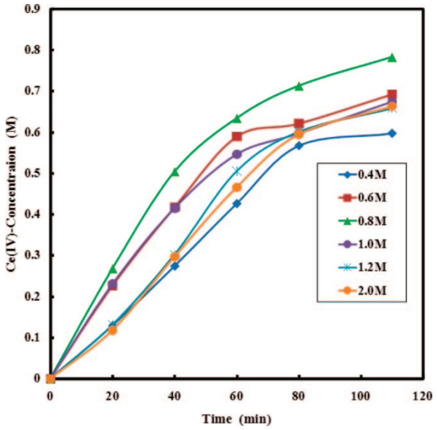

Figure 9. Concentration profiles of Ce(IV) at different Ce(III) concentration with respect to electrolysis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, $d = 5$ A/dm^2, 2 M MSA, 50 °C, 75 rpm].

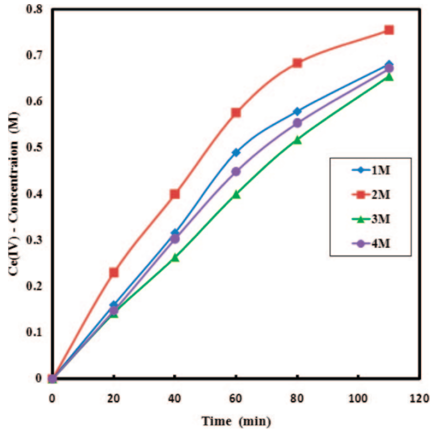

Figure 10. Concentration profiles of Ce(IV) at different Ce(III) concentration with respect to electrolysis time [divided cell, electrodes DSA-O_2SS, volume = 75 mL, $d = 5$ A/dm^2, 0.8 M cerium(III), 50 °C, 75 rpm].

30 °C to 96% at 50 °C. The optimum temperature is 50 °C for Ce(III)/Ce(IV) redox system, and this is an ideal temperature for scale-up and process development studies. It is concluded that the generation of cerium(IV) ion is highly dependent on the electrolysis temperature, that is the conversion is increased with increased temperature.

(e) Effect of Temperature on Cell Voltage. Figure 8 show the influence of temperature on cell voltage for the mediated electrochemical oxidation. The reaction was carried out at a temperature range of 30−50 °C in a batch divided cell. The cell voltage is increased with increased temperature for the generation of cerium(IV) methanesulphonate, and it is found that cell voltage increases slowly with temperature. It is observed that this small amount of increment is due to the high viscous nature of cerium(IV) methanesulphonate solution. During the electrolysis, the electrolyte becomes slurry form at high concentration and this will give the cell voltage rise.

(f) Effect of Cerium(III) Methanesulphonate Concentration. The effects of cerium(III) methanesulphonate concentration were studied from 0.4 to 2.0 M at 5 A/dm^2 current density and 50 °C. Figure 9 Shows the results concentration profiles for the generation of cerium(IV) methanesulphonate at different cerium(III) concentrations. The generation cerium(IV) methanesulphonate is increased with increased cerium(III) methanesulphonate. It can also be observed that increase in concentration of cerium(IV) ions is found to be maximum at a cerium(III) concentration of 0.8 M. From the experimental observation, it also found that at higher concentration of cerium(III), i.e. 1.4−2.0 M, the formed cerium(IV) solution is in high viscous and slurry forms. This type of slurry solution cannot be used for any other applications or reactions. Hence, it is concluded that an 0.8 M cerium(III) concentration having high conversion is suitable for process development.

(g) Effect of Methanesulphonic Acid Concentration. The effects of the methanesulphonic acid on the generation of cerium(IV) ion was investigated. Studies were carried out at different concentration of methanesulphonic acid from 1 to 4 M. The results are presented in Figure 10. It is found that concentration of cerium(IV) formed is increased with increased acid concentration of 2 M methanesulphonic acid and then remains constant on further increase of the acid concentration. It is also found that the concentration of cerium(IV) ions formed increases with increase in duration.

The selection of an acid is very important and plays a key role as the columbic efficiency of the electrochemical cell which depends on the viscosity of the acid employed and hence its mass transfer coefficient. Also, the solubilizing capacity of the acid toward the metal salt is an important consideration. Sulphuric acid possesses low solubility,[14] and moreover, can be used only for partial oxidation of organics. Perchloric acid is explosive in nature. Hydrochloric acid cannot be used because of instability of chloride ion. Nitric acid releases some amount of NOx during the electrolysis preferably at the cathode.

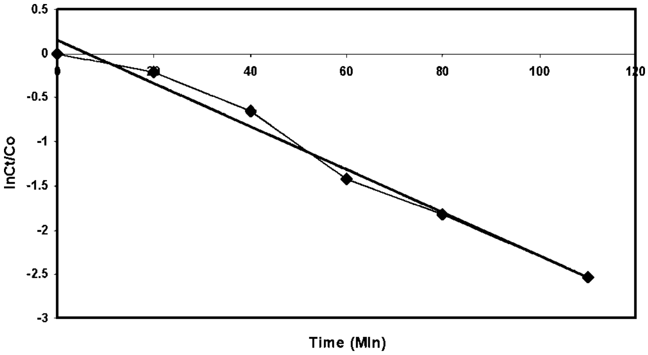

Figure 11. Plot of ln C_t/C_o vs t for the generation of cerium(IV) methanesulphonate.

Scheme 1. Mediated Electro-oxidation System

Anode	6 Ce(III) – $6e^-$	$\xrightarrow{r_1}$	6 Ce(IV)	(1)
	H_2O	$\xrightarrow{r_2}$	$2H^+ + 0.5O_2 + 2e^-$	(2)
Cathode	$6H^+ + 6e^-$	$\xrightarrow{r_3}$	$3H_2$	(3)
Overall	Ce(III) - e^-	$\longrightarrow$	Ce(IV)	(4)
	[A]		[B]	

Therefore, in this study methanesulphonic acid is employed which has low viscosity, good solubility toward cerium salts, and is a good oxidizing agent by itself toward organics.

(h) Kinetics on Electrochemical Preparation of Cerium(IV) Methanesulphonate. Kinetic study was carried out for the electrochemical generation of cerium(IV) methanesulphonate from cerium(III) methanesulphonate at optimized process conditions in methanesulphonic acid medium. The goal of kinetic study is to maximize yield of cerium(IV)methanesulphonate generation by electrochemical method.

Figures 4 and 5 show the concentration profiles of cerium(III) methanesulphonate and cerium(IV) methanesulphonate with respect to time. It can be seen from figures that the concentration of cerium(III) methanesulphonate decreases steadily with time as the concentration of cerium(IV) methanesulphonate increases with time. From the plot of initial concentration [C_o] to final concentration [C_t] of cerium(III) methanesulphonate, the slope of ln[C_t/C_o] vs t gives the rate constant (k; see Figure 11). The linearity of ln C_t/C_o vs t indicates the exponential variation with respect to time, indicating the first order reactions. The value of the rate constant for Ce(III)/Ce(IV) redox system is 0.0008 cm/s.

The reaction steps for the electrochemical generation of cerium(IV) methanesulphonate are given in Scheme 1.

The variation of the amount of specific species in a cell is due to particular electrochemical or chemical reactions. The reactor can be assumed to behave as an ideal stirred tank batch reactor. Denoting reaction rate as r_1 corresponding to each reaction in the scheme, the mass balance can be written as

$$r_2 = 1/0.5\ \mathrm{d}[O_2]/\mathrm{d}t = 1/2\ \mathrm{d}[H^+]/\mathrm{d}t = -\mathrm{d}[H_2O]/\mathrm{d}t \tag{5}$$

$$r_3 = 1/3\ \mathrm{d}[H_2]/\mathrm{d}t = -1/6\ \mathrm{d}[H^+]/\mathrm{d}t \tag{6}$$

$$-\mathrm{d}C_A/\mathrm{d}t = r_1 = \mathrm{d}C_B/\mathrm{d}t \tag{7}$$

where A = Ce(III), B = Ce(IV), r_1 = rate of Ce(IV) generation, r_2 = rate of oxygen formation, and r_3 = rate of hydrogen formation.

Further pseudo-steady-state theory can be applied to for production and consumption of O_2. The rate of formation of O_2 is practically identical to its rate of disappearance. Then writing the rate expression for this system

$$-r_1 = -\mathrm{d}C_A/\mathrm{d}t = kC_A \tag{8}$$

The reactor is an ideal **stirred tank batch reactor**; eq 8 can be integrated to give

$$C_A = C_{Ao}\exp[kt] \tag{9}$$

where C_A = is the concentration of Ce(III) with time in the reactor and C_{Ao} = is the initial concentration of Ce(III) in the reactor.

It is known that the O_2 radical in the bulk is transported to the electrode surface where it undergoes conversion to oxygen, and it is transported back to bulk for reaction. Similarly, Ce(III) is transported from the bulk to the surface for reaction. Assuming that Tafel behavior is applicable

$$\frac{i_1}{2F} = ksSC_{AS}\exp(\beta E) \tag{10}$$

$$\frac{i_1}{2F} = k_LS(C_{Ab} - C_{AS}) \tag{11}$$

$$\frac{i_1}{2Fk_s\exp(\beta E)} = C_{AS} \tag{12}$$

$$\frac{i_1}{2Fk_LS} = C_{Ab} - C_{AS} \tag{13}$$

$$\frac{i_1}{2F}1/k_S\exp(\beta E) + 1/k_LS = kC_{Ab} \tag{14}$$

$$\frac{i_1}{2F}\frac{C_{Ab}}{1/k_S\exp(\beta E) + 1/k_LS} = kC_{Ab} \tag{15}$$

where

$$1/k = 1/k_L + 1/k_S\exp(\beta E) \tag{16}$$

Conclusion

Studies were carried out to find out the optimum process parameters like current density, temperature, cerium(III) methanesulphonate concentration, and methanesulphonic acid concentration for the mediated electrochemical generation of cerium(IV) methanesulphonate from cerium(III) methanesulphonate in a divided batch cell. At optimized process parameters, 97% of conversion and current efficiency were achieved for the conversion of cerium(III) methanesulphonate to cerium(IV) methanesulphonate. The maximum conversion and current efficiency were obtained at a current density of 5 A/dm^2, temperature of 50 °C, and 0.8 M of cerium(III) methanesulphonate concentration in 2 M methane sulfonic acid medium.

Literature Cited

(1) Tilak, B. V. *Technique of Electro organic Synthesis Part-3*; Weinberg, N. L., Ed.; John Wiley and Sons: New York, 1982.

(2) Purgato, F. L. S.; Ferreira, M. I. C.; Romero, J. R. Electrocatalytic oxidation of alcohols, diols and arenes with ceric p-methoxybenzenesulfonate and ceric−p-toluenesulfonate. *J. Mol. Catal. A, Chem.* **2000**, *161*, 99–104.

(3) Cho, L. Y.; Romero, J. R. Chemical and Electrochemical Oxidative Dimerization of Carbonyl Compounds by Cerium(IV) Salts. A Comparative Study. *Tetrahedron Lett.* **1995**, *36*, 8757–8760.

(4) Cho, L. Y.; Romero, J. R. Electro catalytic oxidation of b-dicarbonyl compounds using ceric methanesulphonate as mediator. *Quim. Nova* **1998**, *21*, 144–145.

(5) Cho, L. Y.; Madurro, J. M.; Romero, J. R. Electro oxidation of β-Dicarbonyl Compounds Using Ceric Methanesulphonate as Mediator: Some Kinetics and Spectroscopic Studies. *J. Catal.* **1999**, *186*, 31–45.

(6) Navarrro, M.; DeGiovani, W. F.; Romero, J. R. Electro catalytic oxidation of alcohols and diols using poly pyridyl complexes of ruthenium. Effect of the redox potential on selectivity. *J. Mol. Catal. A, Chem.* **1998**, *135*, 249–256.

(7) Sequeira, C. A. C.; Santos, D. M. F.; Brito, P. S. D. Mediated and non-mediated Electrochemical oxidation of isopropanol. *Appl. Surf. Sci.* **2006**, *252*, 6093–6096.

(8) Galla, U.; Kritzer, P.; Bringmann, J.; Schmieder, H. Process for total degradation of organic wastes by mediated electro oxidation. *Chem. Eng. Technol.* **2000**, *23*, 230–233.

(9) Paulenova, A.; Creager, S. E.; Navratil, J. D.; Wei, Y. Redox potentials and kinetics of the Ce^{3+}/Ce^{4+} redox reaction and solubility of cerium sulfates in sulfuric acid solutions. *J. Power Sources* **2002**, *109*, 431–438.

(10) Fang, B.; Iwasa, S.; Wei, Y.; Arai, T.; Kumagai, M. A study of the Ce(III)/Ce(IV) redox couple for redox flow battery application. *Electrochim. Acta* **2002**, *47*, 3971–3976.

(11) Spotnitz, R. M.; Kreh, R. P.; Lundquist, J. T.; Press, P. J. Mediated electro synthesis with Cerium(IV) in methane sulphonic acid medium. *J. Appl. Electrochem.* **1990**, *20*, 209–215.

(12) Varela, J.; Oberg, S.; Neustedter, T. M.; Nelson, N. Non-thermal organic waste destruction: characterization of the cerox system. *Environ. Prog.* **2001**, *20*, 261–271.

(13) Nelson, N.; Neustedter, T.; Oberg, S.; Varela, J. The cerox process: new technology for organic hazardous waste destruction. In *Symposium on Emerging Technologies: Waste Management in the 21st Century, American Chemical Society Meeting*, San Francisco, 2000.

(14) Wei, Y.; Fang, B.; Arai, T.; Kumagai, M. Electrolytic oxidation of Ce(III) In nitric acid and sulphuric acid media using a flow type cell. *J. Appl. Electrochem.* **2005**, *35*, 561–566.

(15) Raju, T.; Ahmed Basha, C. Electrochemical cell design and development for Mediated electro chemical oxidation—Ce(III)/Ce(IV) system. *Chem. Eng. J.* **2005**, *114*, 55–65.

(16) Liu, Y.; Xia, X.; Liu, H. Studies on cerium (Ce^{4+}/Ce^{3+})–vanadium(V^{2+}/V^{3+}) redox flow cell—cyclic voltammogram response of Ce^{4+}/Ce^{3+} redox couple in H_2SO_4 solution. *J. Power Sources* **2004**, *130*, 299–305.

(17) Randle, T. H.; Kuhn, A. T. The influence of platinum (phase) oxide on the electrode kinetics of the manganese(III)/manganese(II) and cerium (IV)/cerium (III) redox couples in sulphuric acid. *Electrochim. Acta* **1986**, *31*, 739–744.

(18) Balaji, S.; Chung, S. J.; Thiruvenkatachari, R.; Moon, I. S. Mediated electrochemical oxidation process: electro-oxidation of cerium(III) to cerium(IV) in nitric acid medium and a study on phenol degradation by cerium(IV) oxidant. *Chem. Eng. J.* **2007**, *126*, 51–57.

(19) Matheswaran, M.; Balaji, S.; Chung, S. J.; Moon, I. S. Mineralization of phenol By Ce(IV) mediated electrochemical oxidation in methane sulphonic acid medium: A preliminary study. *Chemosphere* **2007**, *69*, 325–331.

(20) Tzedakis, T.; Savall, A. Electrochemical regeneration of Ce(IV) for oxidation of p-methoxytoluene. *J. Appl. Electrochem.* **1997**, *27*, 589–597.

(21) Kiekens, P.; Steen, L.; Donche, H.; Temmerman, E. Kinetics of Ce(IV) reduction at gold, carbon and iridium electrodes. *Electrochim. Acta* **1981**, *26*, 841–845.

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