

# Indirect Electrochemical Oxidation of *p*-Methoxy-Toluene to *p*-Methoxy-Benzaldehyde Using Ceric Methanesulphonate: A Scale-up Study

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Electrochemically produced and regenerated cerium(IV) ions, by  $\text{Ce}^{3+}/\text{Ce}^{4+}$ , are well-known redox mediators and are used particularly as synthesis agents for the indirect oxidation of a side chain methyl group to the aldehyde group in substituted toluene. Detailed studies on indirect electrochemical oxidation of *p*-methoxy-toluene to *p*-methoxy-benzaldehyde using ceric methanesulphonate were carried out. Under optimized conditions, the yield achieved was 65–78% for the oxidation with continuous recycling and electrochemical regeneration of ceric was achieved with a current efficiency of 70–85%. Purity of the product was also remaining consistent during recycling.

## 1. Introduction

The use of the ceric ion as oxidant in organic chemistry is well-known, in chemical literature with numerous applications, for the oxidation of side chain methyl groups to aldehyde groups in polycyclic aromatic hydrocarbons. The mediated electrochemical oxidation (MEO) process with cerium ions is also involved in the electrosynthesis process for the production of several carbonyl compounds commercially and for the destruction of various organic pollutants.<sup>1–16</sup> Industrial applications of this oxidation process however are very limited, because of the high cost of the reagent and difficulties in disposing the effluent. Indirect oxidations using ceric ion have hence been widely studied for the oxidation of organic compounds, since the ceric ions in this process are electrochemically regenerated and recycled. Earlier studies on electrochemical regeneration of ceric ions and oxidation of organic compounds were mostly restricted to sulfuric acid medium. There is also a report on the oxidation of anthracene to anthraquinone using Ce(IV) and Cr(VI) mediators.<sup>17</sup> Apart from anthracene, several aromatic hydrocarbons have also been oxidized (which include *p*-methoxy-toluene) by using ceric ions. There are several reports about the electrochemical oxidation of cerous to ceric in acid media using filter press type flow cells.<sup>1</sup> Dalrymple and Millington have employed divided bipolar cell of plate and frame construction using dished electrodes with Nafion 415 cation exchange membrane as the cell separator and studied the electrochemical oxidation of cerous to ceric in aqueous sulfuric acid medium.<sup>18</sup> Comminellis and Plattner have used parallel plate cell with lead electrodes for the electrochemical oxidation of  $\text{Mn}^{2+}/\text{Mn}^{3+}$  system in sulfuric acid medium.<sup>19</sup>

A large number of redox systems like  $\text{Mn}^{2+}/\text{Mn}^{3+}$ ,  $\text{Co}^{2+}/\text{Co}^{3+}$ ,  $\text{Cr}^{2+}/\text{Cr}^{3+}$ ,  $\text{Cr}^{3+}/\text{Cr}^{6+}$ ,  $\text{Ti}^{3+}/\text{Ti}^{4+}$ ,  $\text{Ce}^{3+}/\text{Ce}^{4+}$ ,  $\text{V}^{4+}/\text{V}^{5+}$ ,  $\text{Pd}^{2+}/\text{Pd}^0$ ,  $\text{Sn}^{4+}/\text{Sn}^{2+}$ ,  $\text{Ag}^{2+}/\text{Ag}^+$ ,  $\text{Cu}^{2+}/\text{Cu}^+$ , and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the form of liquid reagent or as an electrode system are available for carrying out the chemical reaction in a separate chemical reactor and for the electrochemical regeneration and recycle the reagent for further use.<sup>20</sup> The anions employed with Ce(IV) have greatly limited application due to either its instability in the

oxidation process (e.g., chloride), undesired activity with the organic substrates (e.g., chloride, nitrate, perchlorate), or marginal solubility and slow organic oxidations (e.g., sulfate, acetates, trifluoroacetates).

The use of cerium salts of methanesulphonate obviate many of the above problems and yield a high selectivity for a wide range of organic substrates and also enable the recycling of ceric mediator by electrochemical oxidation. The use of ceric methanesulphonate has opened up avenues for the indirect oxidation of substituted toluenes and polycyclic aromatics. Ce(IV) is generally preferred owing to its higher stability and excellent selectivity. Regeneration with good current efficiency and selective organic oxidation with high conversion is achieved by this system. Hence methanesulphonic acid (MSA) is the preferred medium for the electrochemical oxidation of Ce(III) salts. In MSA medium cerium(III) methanesulphonate could also be oxidized in the slurry form in both divided and undivided cells. This process for the indirect oxidation of aromatic compounds via  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox system in MSA has been reported using FM<sub>21</sub> and DEM type cells and achieved around 70% current efficiency for the oxidation.<sup>21–23</sup>

The choice of electrode material is of fundamental importance from an electrochemical point of view. Dimensionally stable anode (DSA) material was widely studied for application in organic oxidation<sup>24–27</sup> and waste treatment systems. The most common DSA material is the  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode, which is extensively used in the chlor-alkali industry for a number of years.<sup>28</sup> DSA has been classified as “active” or “nonactive”, depending on its chemical nature.<sup>29,30</sup> Active electrodes mediate the oxidation of organic species by the formation of higher oxidation state oxides of the metal ( $\text{MO}_{x+1}$ ) whenever such higher oxidation state is reached by the metal oxide (e.g.,  $\text{RuO}_2$  or  $\text{IrO}_2$ ), leading to selective oxidation. Nonactive electrodes present no higher oxidation state available and the organic species is directly oxidized by an adsorbed hydroxyl radical, generally resulting in complete combustion of the organic molecule (e.g.,  $\text{SnO}_2$  or  $\text{PbO}_2$ ).

Mediated electrochemical oxidation (MEO) is a cyclic process involving electrochemical generation of a redox agent and use of that agent to effect a chemical reaction. For an oxidation reaction, the process can be represented schematically as follows:  $\text{R} \rightarrow \text{O} + ne$ ,  $\text{O} + \text{S} \rightarrow \text{P} + \text{R}$ , where R and O represent the mediator in reduced and oxidized state. S and P represent the reactant and the product. Ideally, an electrochemical redox

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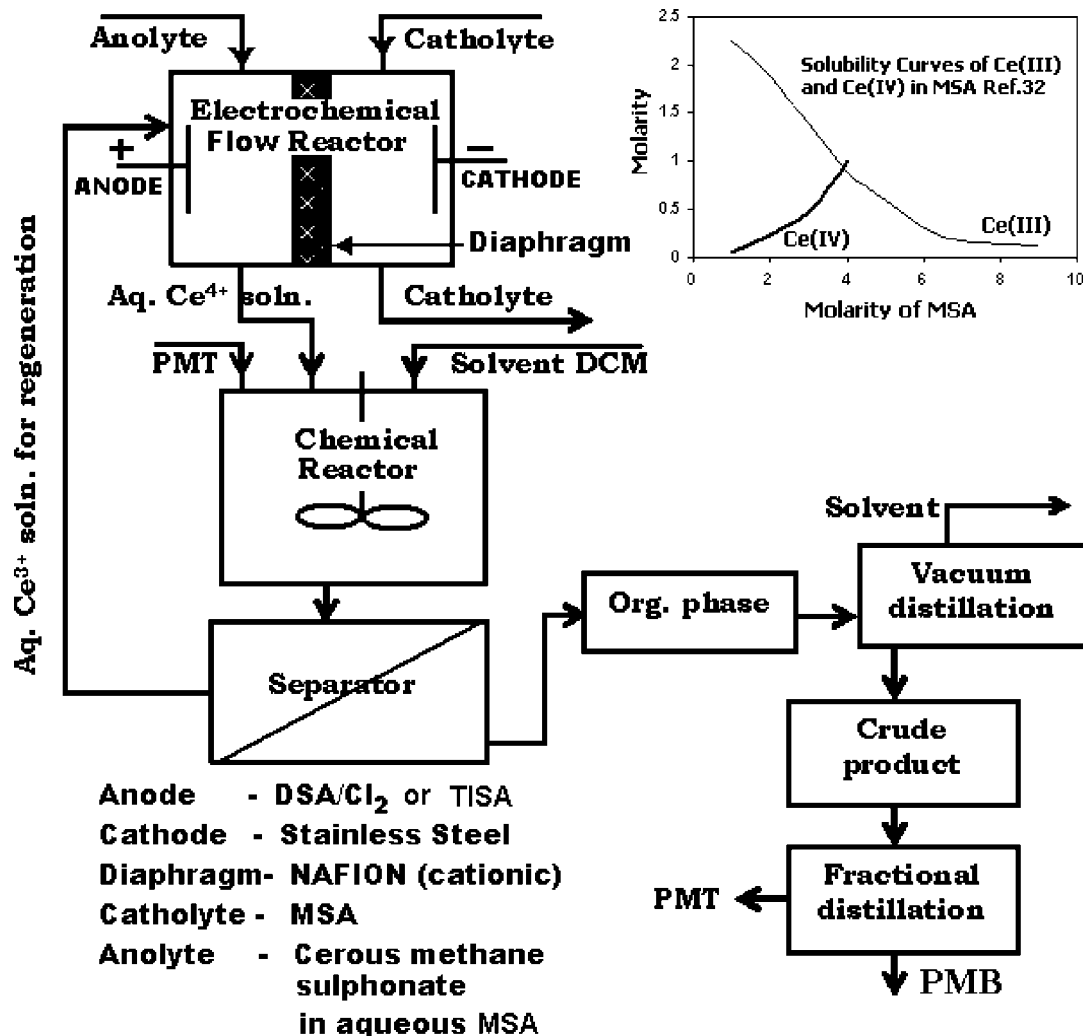


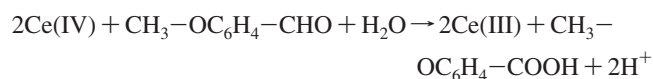
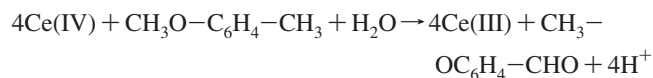
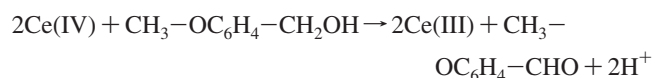
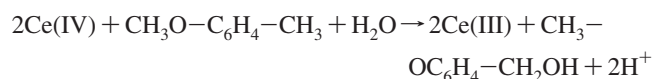
Figure 1. Flowchart of the electrochemical cyclic process.

reaction is reversible and a chemical reaction highly selective. It is advantages to carry out electrochemical and chemical reactions in separate vessels (so-called ex-cell method) so that each step can be standardized independently. For Ce(IV)/Ce(III) system, the reactions that take place in the cell at the anode are  $\text{Ce(III)} \rightarrow \text{Ce(IV)} + e^-$ ,  $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 0.5\text{O}_2 + 2e^-$  (there are two reactions occurring parallel), and at the cathode, the main reaction occurring in acid medium is  $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ . In addition to this there may be cathodic reduction of Ce(IV) that migrated or leaked from anode chamber.

The principal objective of this investigation is to assess that the indirect electrochemical oxidation of *p*-methoxy-toluene (PMT) to *p*-methoxy-benzaldehyde (PMB), using ceric methanesulphonate, which would practicable for scale up as a pollution free viable process since PMB is an important chemical and chemical intermediate in the pharmaceutical and perfumery industry.

In this investigation, by an ex-cell approach, the indirect electrochemical oxidation of PMT to PMB experiments were carried out using ceric mediator in methanesulphonic acid (MSA) medium on the bench and pilot scales (flow type cell). The electrogenerated ceric mediator used for the oxidation of PMT and during chemical oxidation formed cerous ion formed, and it has been regenerated electrochemically and then recycled for chemical oxidation, thereby making it a cyclic process. A flowchart of the electrochemical process is shown in Figure 1. The chemical transformations can be represented as as shown

below, and from the stoichiometric amount of Ce(IV) consumed, the extent of PMB formed can be calculated from the third overall chemical equation:



Cyclic voltammetry (CV) is adopted for the investigation of electrochemical processes over entire potential window available for electro organic synthesis. Hence, a detailed study of the voltammetric behavior of cerous/ceric redox system in MSA medium in the presence and absence of organic reactants was carried out to determine the suitable condition for the electrochemical generation of ceric methanesulphonate.

## 2. Materials and Methods

All the chemicals used were of analytical grade. The cation selective exchange membrane, Nafion 423 (Dupont, USA), was

used as a separator (diaphragm). Solutions of cerous methanesulphonate in aqueous methanesulphonic acid (Analar grade, Ranbaxy, India) were prepared by making a slurry of cerous carbonate,  $Ce_2(CO_3)_3$ , (Indian rare earth) in water and by adding calculated quantity of concentrated MSA to convert cerous carbonate to cerous methanesulphonate and also to maintain the desired MSA concentration in electrolyte. After the reaction, the solution was filtered to remove the insoluble and the clear filtrate was estimated to find out the cerous content by volumetrically.

**2.1. Cyclic Voltammetry.** A single compartment cell with Glassy Carbon, Tokai GC-A type (Tokai Electrode Manufacturing Company Ltd., Japan) as working electrode, platinum as counter electrode, and saturated calomel electrode as a reference electrode were used for CV studies. A potentiostat/galvanostat Model IM6 was used for obtaining voltammograms. The working electrode was fixed in a glass tube using epoxy resins. The electrode area was  $0.0706 \text{ cm}^2$ . The electrical contact of the glassy carbon electrode (GCE) was made through a mercury pool. A standard procedure for pretreatment of electrode was adopted to get reproducible results. The GCE was polished to mirror finish using fine emery paper, and the surface was cleaned by cotton to remove any powdery material on the electrode surface and then degreased thoroughly using trichloroethylene. Then, the electrode was washed with triple distilled water. A mechanically pretreated electrode was then electrochemically activated by dipping in deaerated  $0.1 \text{ mol L}^{-1}$  potassium chloride solution and was activated by electrochemical cycling as described in the literature.<sup>31</sup>

The GCE was potentiodynamically cycled between  $-0.5$  and  $+1.5 \text{ V}$  vs SCE in  $0.1 \text{ mol L}^{-1}$  potassium chloride for about 20–30 min at sweep rate of  $20 \text{ mV s}^{-1}$ . After recording the background current,  $2.0 \text{ mmol L}^{-1}$  potassium ferrocyanide was added and then potential was scanned from  $-0.5$  to  $+0.6 \text{ V}$  to get a reproducible voltammogram of ferrocyanide/ferricyanide system with a  $\Delta E_p$  (peak potential separation) value around 60 mV. Such an activated electrode will be able to give reproducible results for a few hours. For removal of oxygen from electrolyte, nitrogen was used (purified by passing it through a series of wash bottles containing alkaline pyrogallol,  $1.0 \text{ mol L}^{-1}$  sulfuric acid, conductivity water, and molecular sieve, respectively). All the experiments were carried out at  $25 \pm 1 \text{ }^\circ\text{C}$ . In all experiments, the electrochemical cell was washed with nitric acid, distilled water, and finally triple distilled water before recording the cyclic voltammogram. At different sweep rates, CV was obtained for  $34 \text{ mmol L}^{-1}$  cerous methane sulfonate in  $1.0$  and  $4.0 \text{ mol L}^{-1}$  MSA. In addition, voltammograms were also obtained at different time intervals for  $250 \text{ mmol L}^{-1}$  ceric methane sulfonate (containing  $70 \text{ mmol L}^{-1}$  *p*-methoxy-toluene) in dichloromethane at room temperature. Electrochemical activation procedure was adopted whenever the electrode reproducibility was lost. For calculating experimental data, care was taken to detect the background current at each cycle.

**2.2. Bench Scale Study.** **2.2.1. Electrochemical Oxidation.** A 500 mL rectangular cell, with anolyte and catholyte compartment separated by Nafion 423 cation exchange membrane (CXM), was used for electrochemical oxidation. Studies were conducted to evaluate different materials for anode such as platinum, titanium substrate insoluble anodes (TSIA) with an  $RuO_x-IrO_x-TiO_x$  coating,<sup>32</sup> dimensionally stable anode [DSA]/ $O_2$  or [DSA]/ $Cl_2$ , and  $SnO_2/Ti$ . Stainless steel was used as cathode. Cerousmethane sulfonate solution was used as the anolyte and aqueous MSA was used as the catholyte. Electrolysis was carried out to oxidize cerous methanesulphonate to ceric

methanesulphonate at constant current. During electrolysis the ceric ions formed were quantitatively analyzed by titration with ferrous ammonium sulfate using ferroin as an indicator.<sup>33</sup> The current efficiency of electrolysis for the oxidation was calculated from the ratio of ceric ions formed during reaction and the ceric expected based on current passed. Studies were conducted to optimize the electrochemical reaction parameters such as current density, concentration of reactant, acid concentration, temperature, etc.

**2.2.2. Chemical Oxidation.** This process, oxidation of *p*-methoxy-toluene was carried out in a 1 L glass reactor using electrogenerated ceric methanesulphonate in MSA. The aqueous ceric solution and *p*-methoxy-toluene (Analar grade, Merck, India) were taken for the oxidation in the stoichiometry of 4 mol of Ce(IV) for 1 mol of PMT. The electrogenerated ceric solutions and PMT with solvent were taken in a chemical reactor and stirred thoroughly by a mechanical stirrer. The reaction was conducted until there was no more Ce(IV) in the aqueous phase as estimated. Temperature of the reaction was controlled by using a thermostatic water bath. After completion of the reaction, the organic and aqueous phases were separated. The aqueous phase was repeatedly extracted with organic solvent to remove the organic present in the aqueous layer and added to organic layer. The organic layer was then vacuum-distilled to recover the solvent. The residue after distillation contains the product and was analyzed by gas chromatography (GC), Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) spectroscopy with respect to hydrogen (proton-NMR spectra). After separation of the organic phase, the aqueous phase was purified and it was regenerated electrochemically in a divided cell as described earlier. The solvents employed for this process were dichloroethane (DCE; analar grade, Rankem, India) and dichloromethane (DCM; analar grade, Rankem, India).

**2.3. Pilot Scale Study.** For this study, the electrochemical reactor has been designed on the lines of the traditional plate and frame filter press used in chemical industry. The electrochemical cell comprises of parallel plate electrodes, stacked together with an ion exchange membrane or other porous separators by suitably placing them between the electrodes if required. The electrodes and membranes were attached to specially designed injection molded frames made up of polymeric materials such as poly propylene in such a way that the electrolyte is circulated inside the frames between the intervening space between electrodes and membrane. Electrode modules of the desired area were obtained by adding on frames with electrodes and membranes. By connecting several modules in series, cell systems of different sizes were obtained. The cell modules and cell system was designed for continuous process as well as batch operation. In this present study, an electrochemical cell with one anode and two cathodes were used. The geometric dimensions of each of the compartments were  $20 \times 20 \times 1.5 \text{ cm}^3$ . The anode was TSIA with a cathode of stainless steel (of dimensions  $20 \times 20 \times 1.5 \text{ cm}^3$ ). Nafion 423 cation exchange membrane, effective membrane area of  $20 \times 20 \text{ cm}^2$ , was used as a separator (diaphragm). Poly propylene frames were used in the cell arrangements. Electrolysis was carried out in batch mode with circulation of the anolyte and catholyte from separate compartments by Evaki centrifugal pumps.

Chemical oxidation studies were carried out in a glass reactor of 20 L capacity. The reactor was provided with heating mantle for heating the reactor contents. The glass stirrer connected to a geared motor system was used to stir the reactor contents. The speed of the motor was controlled by a dimmer stat. The

reactor outlet was connected to a glass condenser, and the system was also provided with reflux control. The reactor system could be used for both carrying out chemical oxidation and for simple distillation. The products obtained were characterized by GC.

### 3. Results and Discussion

**3.1. Cyclic Voltammetry.** In cyclic voltammetric studies, both the electrodes and electrolyte are kept stationary and thus no convective mass transfer is involved. But since the potential varies with time, the surface concentration also depends on time hence the Fick's second law of diffusion,  $\partial C_R/\partial t = D_R \partial^2 C_R/\partial x^2$ , is solved to estimate the surface concentration. For the irreversible electron transfer process ( $Ce^{3+} \rightarrow Ce^{4+} + e^-$  or  $R \rightarrow O + ne$ ), one of the boundary conditions used for solving the above diffusion equation is, i.e., at electrode surface  $t > 0$ ;  $x = 0$ ;  $D_R \partial C_R/\partial x = k_f C_R^b$  and  $k_f = k_f^0 e^{bE}$ . The irreversible reaction peak potential is also sweep rate dependent is given by<sup>34</sup>

$$E_p = E^0 + (RT/\alpha nF) \ln[(k_f^R/D_R)^{1/2} - 0.5 \ln(\alpha nFv/RT) - 0.78]$$

The peak current for reversible and irreversible processes are given by

$$i_p = 2.69 \times 10^5 n^{3/2} C_R^b D_R^{1/2} v^{1/2}$$

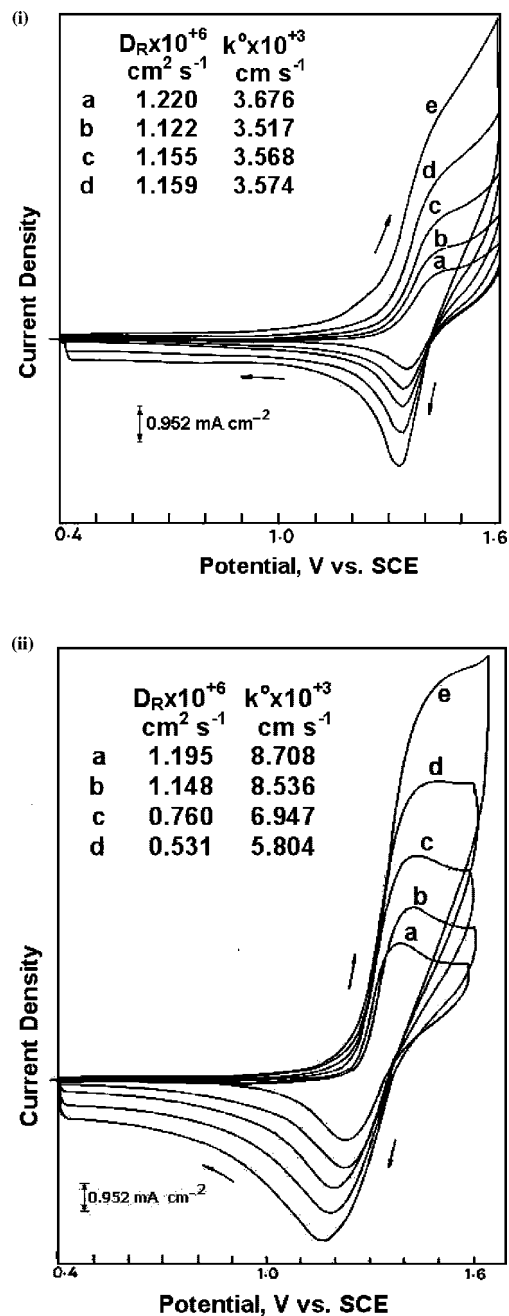
$$i_p = 2.69 \times 10^5 n(\alpha n)^{1/2} C_R^b D_R^{1/2} v^{1/2}$$

The peak separation is defined as  $\Delta E_p = E_{p,a} - E_{p,c}$ . Nicholson<sup>34</sup> has tabulated for each  $\Delta E_p$  value a corresponding parameter  $\Psi$ , given by the following equation:

$$\Psi = \frac{(D_R/D_O)^{\alpha/2} k_f^0}{(D_R \pi n F v / RT)^{1/2}}$$

Then, knowing  $\Delta E_p$ ,  $k_f^0$  and  $D_R$  can be evaluated. The voltammetric behavior of Ce(IV)/Ce(III) redox system in methanesulphonic acid medium was investigated at low as well as high acid concentrations.

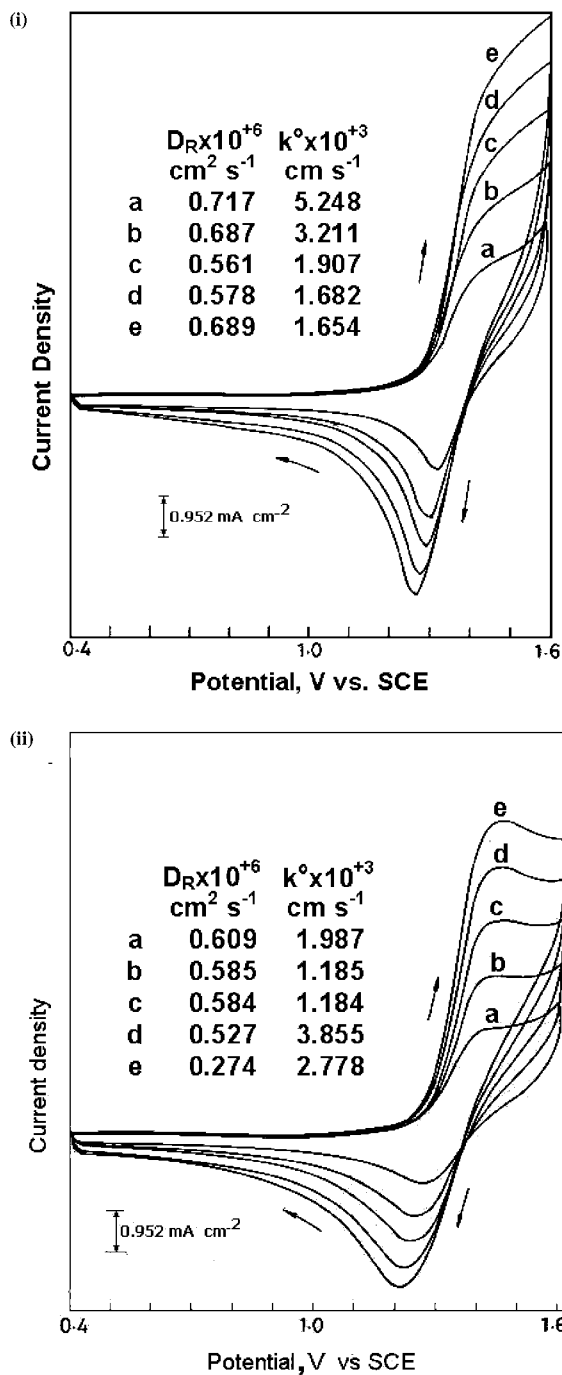
Typical cyclic voltammogram of electrochemical oxidation was obtained for 34 mmol L<sup>-1</sup> cerous methanesulphonate at different concentration of MSA and sweep rates are shown in Figure 2. A distinct oxidation wave as well as reduction peaks were observed in each of the voltammogram. The peak currents increase with sweep rate.  $D_R$  and  $k_f$  were computed using the peak current and peak potential characteristics of CV behavior and the data were presented in the figure itself. It is observed that both peak currents increased with concentration as well as with sweep rate. From the CV obtained, the anodic peaks are more distinctly visible in 4.0 mol L<sup>-1</sup> MSA (Figure 2ii) as compared to 1.0 mol L<sup>-1</sup> MSA (Figure 2i). Figure 3 is the recorded cyclic voltammograms at the sweep rate 40 mV s<sup>-1</sup> indicating the effects of concentration of cerous methanesulphonate in 1.0 and 4.0 mol L<sup>-1</sup> MSA. It is observed that both peak currents increase with concentration as well as sweep rate. The voltammetric behavior in cerous methanesulphonate in different acid concentrations reveals that the voltammograms are quite similar (as shown in Figures 3i and 3ii). The peak potential values and  $\Delta E_p$  values are also quite comparable. The diffusion coefficient of Ce<sup>3+</sup> and the electrochemical rate constant of the redox couple Ce<sup>4+</sup>/Ce<sup>3+</sup> determined from the cyclic voltammetry measurements obtained at different conditions the data are presented in the figure itself. The anodic peak current tends to decrease slightly with increasing MSA concentration. This might be due to the change in diffusion coefficient of Ce(III) species or to some other blocking effects. Earlier studies have also indicated that Ce(IV)/Ce(III) redox couple give a well



**Figure 2.** Typical cyclic voltammogram of electrochemical oxidation of Ce(III) on GCE at different concentrations of MSA and sweep rates: (i) 34 mmol L<sup>-1</sup> Ce(III) in 1.0 mol L<sup>-1</sup> MSA (sweep rates (a) 10, (b) 20, (c) 40, (d) 80, (e) 160 mV s<sup>-1</sup>); (ii) 34 mmol L<sup>-1</sup> Ce(III) in 4.0 mol L<sup>-1</sup> MSA (sweep rates (a) 10, (b) 20, (c) 40, (d) 80, (e) 160 mV s<sup>-1</sup>).

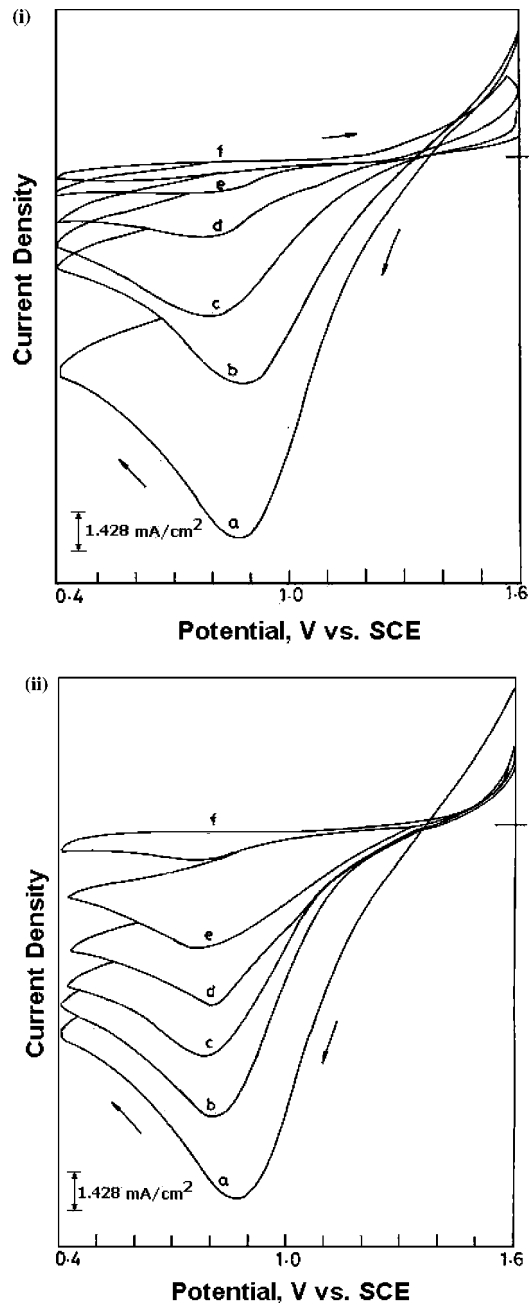
defined responses in MSA medium in the concentration range of 1.0–8.0 mol L<sup>-1</sup> MSA.<sup>35</sup>

Some experiments were also carried out to find out the oxidizability of PMT using ceric methanesulphonate. For these experiments electrogenerated ceric methanesulphonate stock solutions were employed. The reactants dissolved in dichloromethane/dichloroethane were used in the voltammetric studies to ensure the miscibility of reactant with redox mediator. The concentration of solvent in the electrolyte solution was maintained around 10%, which only meant for the organic phase present in the chemical reaction system. Typical cyclic voltammogram obtained at different time intervals for 250 mmol L<sup>-1</sup> ceric methanesulphonate containing 70 mmol L<sup>-1</sup> *p*-methoxy-toluene (in dichloromethane) at room temperature are



**Figure 3.** Typical cyclic voltammogram of electrochemical oxidation of Ce(III) at  $40 \text{ mV s}^{-1}$  on GCE in different concentrations of Ce(III) and MSA: (i) Ce(III) (a) 34, (b) 96, (c) 125, (d) 152  $\text{mmol L}^{-1}$  in  $1.0 \text{ mol L}^{-1}$  MSA; (ii) Ce(III) (a) 34, (b) 66, (c) 96, (d) 125, (e) 152  $\text{mmol L}^{-1}$  in  $4.0 \text{ mol L}^{-1}$  MSA.

shown in Figure 4i. The ceric methanesulphonate concentration decreases substantially with time and the reaction is completed within 35 min. The same experiments were also repeated at  $15^{\circ}\text{C}$ , and it was observed that the ceric methanesulphonate concentration decreases much slower with time and takes nearly 65 min for completion. The voltammograms are shown in Figure 4ii. The variations of cathodic peak current with time for *p*-methoxy-toluene at these two temperatures are also compared in Figure 5. These results clearly suggest the possibility of using cyclic voltammetry for the assessment of the oxidizability of organic compounds.



**Figure 4.** Typical cyclic voltammogram of  $250 \text{ mmol L}^{-1}$  Ce(IV) in  $1 \text{ mol L}^{-1}$  MSA and  $70 \text{ mmol L}^{-1}$  of PMT recorded at  $40 \text{ mV s}^{-1}$  for different temperature and time intervals: (i) At  $30^{\circ}\text{C}$  (a) 0, (b) 3, (c) 6, (d) 12, (e) 25, (f) 35 min; (ii) At  $15^{\circ}\text{C}$  (a) 0, (b) 5, (c) 10, (d) 20, (e) 40, (f) 65 min.

**3.2. Investigations of Bench Scale Setup. 3.2.1. Electrochemical Oxidation of Ce(III) to Ce(IV) in MSA.** By the review of literature and from the voltammetric studies, it is observed that the ceric ions are a promising mediator for the selective oxidation of organic compounds. Hence detailed studies were carried out to evaluate the various conditions for the electro-generation of ceric methanesulphonate, and the results are reported in this section. The solubility of cerous and ceric in MSA medium is reported in the literature<sup>36</sup> as indicated in the Figure 1. The Ce(III) concentration decreasing with increasing concentration of MSA, while the solubility of Ce(IV) increasing with acid concentration and is limited at lower concentration of MSA. Thus electrochemical generation of Ce(IV) at low acid concentration are producing slurry, and it could to be used for the oxidation of organic compounds. However, Ce(IV) was

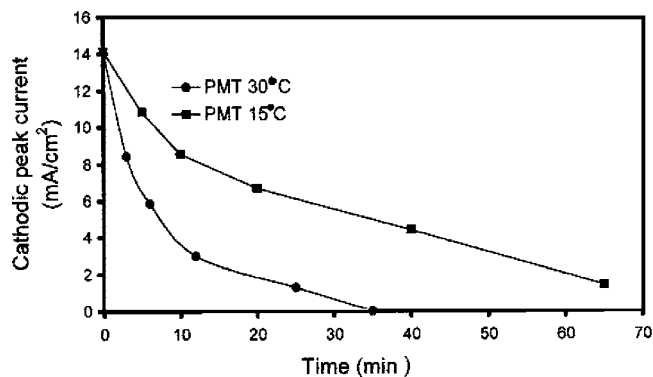


Figure 5. Depletion of cathodic peak of ceric ion in reaction with PMT at 30 and 15 °C. (acid concentration 1.0 mol L<sup>-1</sup> MSA, sweep rate 40 mV s<sup>-1</sup>).

Table 1. Electrochemical Oxidation of Ce(III) to Ce(IV) in Aqueous MSA in a Batch Divided Cell: Effect of Anode Material<sup>a</sup>

anode material	current density (A dm <sup>-2</sup> )	cell voltage (V)	conc of Ce(IV) formed (mol L <sup>-1</sup> )	current efficiency (%)
platinum 0.48 dm <sup>2</sup>	2.0	2.5–4.2	0.960	95.9
	3.0	2.5–4.5	0.900	89.9
	4.0	2.5–4.5	0.875	87.5
	5.0	2.5–4.5	0.850	85.0
	6.0	2.5–5.5	0.830	83.0
	8.0	3.0–6.0	0.760	75.9
TSIA 0.45 dm <sup>2</sup>	10.0	3.0–6.5	0.710	71.0
	2.0	2.5–3.5	0.863	85.3
	3.0	2.7–4.0	0.840	84.1
	4.0	3.0–4.2	0.830	83.8
	5.0	3.0–4.5	0.800	80.2
	6.0	3.2–4.8	0.770	76.9
DSA/O <sub>2</sub> 0.46 dm <sup>2</sup>	8.0	4.0–6.5	0.700	70.2
	10.0	4.0–7.5	0.600	60.3
	2.0	2.5–3.5	0.810	81.1
	3.0	3.0–4.0	0.770	77.2
	4.0	3.0–3.5	0.735	73.6
	5.0	3.5–5.0	0.696	69.5
SnO <sub>2</sub> /Ti 0.47 dm <sup>2</sup>	6.0	3.5–6.5	0.633	63.4
	8.0	4.0–6.5	0.597	59.7
	10.0	4.0–6.5	0.527	52.8
	2.0	3.0–4.0	0.760	76.2
	3.0	3.0–4.5	0.700	70.1
	4.0	3.0–5.0	0.640	64.3
	5.0	3.5–7.5	0.510	51.1
	6.0	3.5–7.5	0.441	44.2
	8.0	4.0–8.0	0.381	38.2
	10.0	4.0–9.0	0.293	29.3

<sup>a</sup> Conditions: anolyte 1.0 mol L<sup>-1</sup> Ce(III) in 2.0 mol L<sup>-1</sup> MSA, catholyte 2.0 mol L<sup>-1</sup> MSA, current passed theoretical.

obtained in solutions at higher MSA concentration but due to the limited solubility of Ce(III) at high acid concentration, the electrolysis carried out with higher degree of conversion to get the same ceric concentration. Hence, detailed studies for evaluation were carried out at varying acid concentrations.

**Effect of Anode Material.** Electrochemical oxidation of Ce(III) to Ce(IV) was carried out using divided type of cells at room temperature at constant current density of 5.0 A dm<sup>-2</sup> and 2.0 mol L<sup>-1</sup> MSA as anolyte and as catholyte were to evaluate the effect of electrode materials on the current efficiency for ceric generation. The concentration of Ce(III) was maintained at 1.0 mol L<sup>-1</sup>. Electrolysis was conducted for theoretical time and the results are reported in Table 1. It is seen from the table that ceric generation occurs at high current efficiency on a wide range of electrode materials.

The platinum anode gives a high current efficiency (more than 80%) while the catalytic electrodes such as TSIA and DSA/

Table 2. Comparison of Different Electrode Material for Ceric Generation under Optimized Conditions<sup>a</sup>

expt no.	electrode material	current efficiency (%)	specific energy consumption (kW h kg <sup>-1</sup> )
1.	platinum	85.0	0.787
2.	TSIA	80.2	0.896
3.	DSA/O <sub>2</sub>	69.5	1.167
4.	SnO <sub>2</sub> /Ti	51.1	2.061

<sup>a</sup> Conditions: current density 5.0 A dm<sup>-2</sup>. Other conditions are as described in Table 1.

O<sub>2</sub> give higher current efficiencies of (70–80%) and the SnO<sub>2</sub>/Ti electrode gives a lower current efficiency (50%). From the practical point of view, the catalytic electrodes are preferred as of their availability in standard sizes and of their comparative low cost.

**Effect of Current Density.** The effect of anodic current density on current efficiency for ceric generation was studied using platinum anode and also other catalytic anodes such as TSIA, DSA/O<sub>2</sub>, and SnO<sub>2</sub>/Ti. The results are reported in Table 1. It is seen from the table that the ceric generation could be conducted at Pt anode with higher current efficiency at current density up to 10.0 A dm<sup>-2</sup>. TSIA, DSA/O<sub>2</sub>, and SnO<sub>2</sub>/Ti anodes gave lower current efficiencies at higher current density, and the optimum current density with catalytic anodes was around 5.0 A dm<sup>-2</sup>. A comparison of the different electrode materials for ceric generation under optimized conditions is shown in Table 2. From the results obtained, it is observed that current efficiency was higher with platinum anodes and energy consumption was lower. TSIA and DSA/O<sub>2</sub> could be used for ceric oxidation and choice can be made based on the stability of electrode materials at high acid concentrations.

**Effect of Acid Concentration.** TSIA and DSA/O<sub>2</sub> anodes were taken up for further detailed optimization studies, in view of the availability as the standard electrode material for commercial scale electrochemical reactor. Studies were conducted to evaluate the effect of MSA concentration on ceric generation and the results are reported in Table 3. It is seen from Table 3 that ceric ions could be generated at higher yield and with remarkable current efficiency in the acid concentrations from 1.0 to 6.0 mol L<sup>-1</sup>. Current efficiency was decreasing marginally at further higher acid concentration. Voltage variations were not significant. Results obtained with DSA/O<sub>2</sub> anodes showed that current efficiencies for ceric generation are similar that of TSIA anode.

**Effect of Ce(III) Concentration.** The advantages of using Ce(III)/Ce(IV) mediator is its good solubility and stability at varying acid concentrations. Effect of Ce(III) concentration on current efficiency for ceric generation was studied using TSIA and DSA/O<sub>2</sub> anodes and the results are reported in Table 4. The studies were conducted at the optimum current density of 5.0 A dm<sup>-2</sup> and at a constant acid concentration of 2.0 mol L<sup>-1</sup> MSA. It is seen from the table that the ceric can be generated at concentrations ranging from 0.18 to 0.91 mol L<sup>-1</sup> with both TSIA and DSA/O<sub>2</sub> anodes. At higher ceric concentration, the ceric is produced in the slurry form due to the lower solubility of ceric at lower acid concentration. The ceric slurries could be used for chemical oxidations and the reduced Ce(III) ions have higher solubility and would be in the solution form after oxidation of the organic reactant.

**3.2.2. Indirect Oxidation Using Ceric Methanesulphonate. *p*-Methoxy-Toluene to *p*-Methoxy-Benzaldehyde.** Ceric ions mediated oxidation of *p*-methoxy-toluene has been well studied. Kreysa and Medin<sup>4</sup> used ceric sulfate in aqueous sulfuric acid medium to oxidize *p*-methoxy-toluene in dichloromethane. There are also some

**Table 3. Effect of Acid Concentration on Electrochemical Oxidation of Ce(III) to Ce(IV) Using TSIA and DSA/O<sub>2</sub> Anodes<sup>a</sup>**

anode material	conc of Ce(III) taken for oxidn (mol L <sup>-1</sup> )	conc of MSA (mol L <sup>-1</sup> )	total charge passed (A h)	cell voltage (V)	conc of Ce(IV) formed (mol L <sup>-1</sup> )	current efficiency (%)
TSIA 0.45 dm <sup>2</sup>	0.52	1.0	5.57	2.5–3.5	0.427	82.2
	0.51	2.0	5.46	2.5–3.5	0.415	81.5
	0.50	4.0	5.36	3.0–4.5	0.371	74.3
	0.50	5.0	5.36	3.0–6.0	0.358	71.6
	0.45	6.0	4.82	3.0–6.5	0.310	68.6
DSA/O <sub>2</sub> 0.46 dm <sup>2</sup>	0.52	1.0	5.57	2.5–3.5	0.41	78.8
	0.51	2.0	5.46	2.5–3.5	0.38	75.6
	0.50	4.0	5.36	3.0–5.5	0.35	71.2
	0.50	5.0	5.36	3.0–6.0	0.32	64.3
	0.45	6.0	4.82	3.0–6.5	0.27	60.2

<sup>a</sup> Conditions: catholyte aqueous MSA (1.0–6.0 mol L<sup>-1</sup>), current density 5.0 A dm<sup>-2</sup>.

**Table 4. Effect of Ce(III) Concentration on Electrochemical Oxidation of Ce(III) to Ce(IV) Using TSIA and DSA/O<sub>2</sub> Anodes<sup>a</sup>**

anode material	conc of Ce(III) taken for oxidn (mol L <sup>-1</sup> )	total charge passed (A h)	cell voltage (V)	conc of Ce(IV) formed (mol L <sup>-1</sup> )	current efficiency (%)
TSIA 0.45 dm <sup>2</sup>	0.25	2.68	2.0–3.0	0.180	72.30
	0.50	5.36	2.0–3.5	0.373	74.50
	0.75	8.04	3.0–4.0	0.477	79.62
	1.00	10.72	3.0–4.5	0.800	80.20
	1.25	13.40	3.0–6.0	0.918	73.50
DSA/O <sub>2</sub> 0.46 dm <sup>2</sup>	0.25	2.68	2.5–3.5	0.175	70.10
	0.50	5.36	2.5–3.5	0.380	75.60
	0.75	8.04	3.5–5.0	0.540	71.85
	1.00	10.72	3.5–5.0	0.696	69.50
	1.25	13.40	3.5–6.5	0.780	62.20

<sup>a</sup> Conditions: catholyte 2.0 mol L<sup>-1</sup> MSA, anolyte acid conc. 2.0 mol L<sup>-1</sup> MSA, current density 5.0 A dm<sup>-2</sup>.

**Table 5. Indirect oxidation of *p*-Methoxy-Toluene to *p*-Methoxy-Benzaldehyde: Effect of Temperature<sup>a</sup>**

expt no.	amount of Ce(IV) taken for oxidn (g)	amount of PMT taken for oxidn (g)	solvent <sup>b</sup>	temp (°C)	reaction time		amount of PMB formed (g)	aldehyde content (%) by GC	material yield (%)
					hour	minute			
1	22.37	4.86	DCM	5–10	2	30	5.10	80.23	75.77
2	21.27	4.62	DCM	15–20	2	10	5.02	81.25	79.35
3	22.12	4.81	DCM	25–30	1	40	5.00	88.00	82.08
4	20.28	4.41	DCE	35–40	1	15	5.00	77.82	79.24
5	22.17	4.82	DCE	50–55	0	25	5.10	66.20	62.70

<sup>a</sup> Conditions: oxidant 325 mL ceric methane-sulphonate (0.5 mol L<sup>-1</sup>) in 1.0 mol L<sup>-1</sup> MSA. <sup>b</sup> DCM = dichloromethane. DCE = dichloroethane.

**Table 6. Effect of Solvent<sup>a</sup>**

expt no.	amount of Ce(IV) taken for oxidn (g)	amount of PMT taken for oxidn (g)	solvent	reaction time		amount of PMB formed (g)	aldehyde content (%) by GC	material yield (%)
				hour	minute			
1	22.13	4.81	DCM	1	40	5.00	88.00	82.00
2	22.20	4.83	DCE	1	30	4.98	79.63	73.42
3	20.42	4.44	cyclo-hexane	0	30	3.50	12.50	8.10

<sup>a</sup> Condition: oxidant 325 mL of ceric methanesulphonate in 1.0 mol L<sup>-1</sup> MSA, temperature 25–30 °C.

**Table 7. Effect of Acid Concentration<sup>a</sup>**

expt no.	amount of Ce(IV) taken for oxidn (g)	amount of PMT taken for oxidn (g)	acid conc (mol L <sup>-1</sup> )	reaction time		amount of PMB formed (g)	aldehyde content (%) by GC	material yield (%)
				hour	minute			
1	22.25	4.83	0.5	2	25	5.00	75.50	70.16
2	21.82	4.75	1.0	1	40	4.86	88.08	80.90
3	21.95	4.78	2.0	1	00	4.82	70.21	63.60
4	22.16	4.81	4.0	0	35	4.86	66.25	60.20

<sup>a</sup> Conditions: oxidant 325 mL of ceric methane-sulphonate (≈ 0.5 mol L<sup>-1</sup>), solvent dichloromethane, temperature 25–30 °C.

reports for the same compound. A complete kinetic study of the various steps in the oxidation of *p*-methoxy-toluene has also been reported.<sup>7</sup> Recently Tzedakis and Savall have reported the indirect oxidation of *p*-methoxy-toluene to *p*-methoxy-benzaldehyde by ceric sulfate on platinised titanium electrode.<sup>9</sup> The use of ceric sulfate for indirect

oxidation needs handling of large volumes of the oxidant solution in view of the lower solubility of ceric in sulfuric acid medium. In the present studies, results are reported on the indirect oxidation of *p*-methoxy-toluene using ceric methanesulphonate. The oxidation of *p*-methoxy-toluene was carried out in a glass reactor of 1.0 L capacity

**Table 8. Recycling under Optimum Conditions<sup>a</sup>**

expt no.	amount of Ce(IV) taken for oxidn (g)	amount of PMT taken for oxidn (g)	amount of PMB formed (g)	aldehyde content (%) by GC	material yield (%)	ceric regeneration (g)
1	22.28	4.845	5.00	87.2	80.74	20.10
2	reuse 1	4.350	4.67	79.8	76.90	18.12
3	reuse 2	3.940	4.52	66.2	68.00	16.42 <sup>b</sup>
4	reuse 3	5.000	5.06	78.1	70.90	20.25
5	reuse 4	4.840	5.06	77.8	79.10	17.21 <sup>b</sup>

<sup>a</sup> Oxidant 325 mL of ceric methane-sulphonate in 1.0 mol L<sup>-1</sup> MSA, solvent dichloromethane, temperature 25–30 °C, acid 1.0 mol L<sup>-1</sup> MSA. <sup>b</sup> The regenerated ceric amounts to 23.08 g by the addition of Ce(IV) salt.

**Table 9. Electrochemical Oxidation of Cerous to Ceric in MSA Medium Using Flow Cells<sup>a</sup>**

no.	conc of Ce <sup>3+</sup> taken for oxidation (mol L <sup>-1</sup> )	conc of acid (mol L <sup>-1</sup> )	current density (A dm <sup>-2</sup> )	cell voltage (V)	total charge passed (A h)	conc of Ce <sup>4+</sup> formed (mol L <sup>-1</sup> )	current efficiency (%)	specific energy consumption (kW h kg <sup>-1</sup> )
1	1.60	1.0	2.50	4.0	110.0	1.23	94.70	0.81
2	1.20	1.0	2.50	4.5	57.3	0.52	87.42	0.98
3	0.85	1.0	3.75	2.5	112.5	0.49	60.28	0.84
4	1.10	1.0	7.50	4.0	88.2	0.38	33.80	2.26
5	0.85	2.0	4.00	3.8	68.0	0.53	62.66	1.18
6	0.70	2.0	5.00	3.2	63.6	0.52	73.79	0.82
7	1.25	2.0	5.00	4.0	132.0	0.77	63.11	1.21

<sup>a</sup> Anode TSIA (8.0 dm<sup>2</sup>), cathode stainless steel (8.0 dm<sup>2</sup>), anolyte cerous methanesulphonate in aqueous MSA, type of cell flow cell, diaphragm NAFION exchange membrane (cationic), temperature 30–35 °C.

**Table 10. Oxidation of *p*-Methoxy-Toluene to *p*-Methoxy-Benzaldehyde in a 20 L Reactor<sup>a</sup>**

vol (L)	amount of Ce <sup>4+</sup> taken for oxidation (g)	amount of Ce <sup>3+</sup> present (g)	amount of PMT taken (g)	reaction time		wt of residue after distillation (g)	aldehyde content as per GC (%)	yield of aldehyde based on raw material (%)
				hour	minute			
6.00	415.0		82.00	2	15	84.40	83.9	78.09
5.50	363.0	21.4	72.00	2	55	75.30	76.8	71.46
4.62	353.0	29.5	67.83	3	30	70.20	81.8	75.94
5.00	390.3	9.8	77.50	3	55	81.40	72.8	68.56
4.60	358.9	20.8	67.83	3	55	69.22	79.7	72.95
4.40	311.2	39.5	58.14	3	35	60.32	71.2	66.27
4.62	295.5	35.1	53.00	4	20	58.14	74.1	72.93

<sup>a</sup> Reactor 20 L glass reactor fitted with heating mantle and stirrer with reflux condenser, oxidant ceric methanesulphonate solution in 1.0 mol L<sup>-1</sup> MSA, solvent dichloromethane, temperature 25–30 °C.

**Table 11. Electrochemical Regeneration of Ceric after Chemical Oxidation<sup>a</sup>**

no.	input Ce <sup>3+</sup> (g)	total charge passed (A h)	output		current efficiency (%)	specific power consumption (kW h kg <sup>-1</sup> )
			Ce <sup>4+</sup> (g)	Ce <sup>3+</sup> (g)		
1	402.4	82.0	363.0	21.4	84.62	0.98
2	398.7	87.0	353.0	29.5	77.56	0.80
3	378.8	94.5	355.9	10.4	71.99	1.02
4	395.5	90.1	357.8	21.8	75.91	1.10
5	365.8	84.5	333.0	16.9	75.33	1.12
6	340.9	73.3	310.3	21.8	80.92	0.97

<sup>a</sup> Conditions are as described in Table 9.

as described earlier. Studies were conducted to evaluate the optimum reaction condition such as reaction temperature, acid concentration, etc. to get high yield and good selectivity for *p*-methoxy-benzaldehyde.

The residue obtained from the chemical reaction was again fractionated and the pure product was subjected to FTIR and proton-NMR analysis. A strong absorption at 1693.94 cm<sup>-1</sup> was noticed in the FTIR spectrum of the isolated product which corresponds to aldehyde group of *p*-methoxy-benzaldehyde. Typical proton-NMR of the synthesized sample showed a single peak at  $\delta = 9.8$ (s) ppm corresponds to the aldehyde proton. The absorption corresponding to the aromatic proton is observed in the region of 7.0(d) and 7.8(d) ppm. Methoxy proton is observed at 3.9(s) ppm.

**Effect of Temperature.** Chemical reactions were conducted to study the effect of temperature on the oxidation of *p*-methoxy-toluene to *p*-methoxy-benzaldehyde. Studies were carried out

at constant acid concentration of 1.0 mol L<sup>-1</sup> MSA. Dichloromethane and dichloroethane were used as a solvent. The results are reported in Table 5. It is seen from the table that the aldehyde yield decreases with increasing temperature and 25–30 °C appears to be the optimum temperature for the oxidation. The aldehyde content of the product was around 75–80% under optimum temperature. Reaction time decreases with increasing temperature. At high temperature, the acid formation was higher.

**Effect of Solvent.** Studies were conducted at an optimum temperature of 25–30 °C using different solvents. The results are reported in Table 6. It is observed from Table 8 that dichloromethane and dichloroethane gave nearly identical results, but with cyclohexane as a solvent, the fact that the selectivity of the aldehyde is low may be due to the less polar nature of the solvent.

**Effect of Acid Concentration.** Methanesulphonic acid concentration is another important parameter in the redox mediated indirect oxidation. Studies were conducted to observe the effect of MSA concentration on the partial oxidation of *p*-methoxy-toluene to *p*-methoxy-benzaldehyde. The results are reported in Table 7. It is observed from the table that partial oxidation of *p*-methoxy-toluene to *p*-methoxy-benzaldehyde is favored with the use of lower acid concentration around 1.0 mol L<sup>-1</sup> MSA. At higher acid concentration, the acid formation is more. 1.0 mol L<sup>-1</sup> acid concentration appears to be the optimum acid concentration.

**Studies under Optimum Conditions.** A few reactions were conducted for the oxidation of *p*-methoxy-toluene to *p*-methoxy-



Table 12. Material Balance

reactor	input	output
electrochemical reactor	anolyte Ce <sup>3+</sup> 402.2 g in MSA catholyte Ce <sup>3+</sup> 0.0 g in 1 mol L <sup>-1</sup> MSA	Ce <sup>3+</sup> 21.4 g, Ce <sup>4+</sup> 363.0 g Ce <sup>3+</sup> 17.9 g
chemical reactor	Ce <sup>3+</sup> 21.4 g, Ce <sup>4+</sup> 363.0 g, PMT 72 g in DCM 750 mL	aldehyde yield 71.46, Ce <sup>3+</sup> 384.4 g
electrochemical reactor	anolyte Ce <sup>3+</sup> 384.4 g catholyte 17.9 g	Ce <sup>3+</sup> 15.2 g, Ce <sup>4+</sup> 353.0 g 34.1 g

benzaldehyde under optimized concentration with continuous recycling of the regenerated ceric methanesulphonate. The results are reported in Table 8. Almost identical yields were obtained (75–80%) with recycling the oxidant. This reaction has been taken up for scale-up studies, and the results are discussed in the following section.

**3.3. Scale-up Studies. 3.3.1. Electrochemical Oxidation of Cerous to Ceric using Electrochemical Flow Cell.** Trials were conducted for the electrochemical oxidation of cerous to ceric using the electrochemical flow cell described earlier. TSIA (8.0 dm<sup>2</sup>) was used as anode and stainless steel (8.0 dm<sup>2</sup>) as cathode. Studies were conducted using 1.0 and 2.0 mol L<sup>-1</sup> MSA as the electrolyte. Cerous concentration in the trials varied from 0.7 to 1.6 mol L<sup>-1</sup>. Electrolysis temperature was maintained at 30–35 °C. The oxidation of *p*-methoxy-toluene was restricted to the optimum concentration of MSA between 1.0 and 2.0 mol L<sup>-1</sup>. The capacity anolyte and catholyte were recirculated at a flow rate 2.0 L min<sup>-1</sup>. The reservoir capacity catholyte was 2 L whereas that of anolyte was 10 L. Using 1.0 mol L<sup>-1</sup> MSA as electrolyte electrochemical oxidation studies were conducted at current densities from 2.5 to 7.5 A dm<sup>-2</sup>. The results are reported in Table 9 (trials 1–4). It is seen from the table that current efficiency decreases with increasing current density. High ceric concentration up to 1.2 mol L<sup>-1</sup> (ceric salt and ceric in solution) could be generated with high current efficiencies, and the specific energy consumption was between 0.8 to 2.26 kW h kg<sup>-1</sup>. Results of the studies conducted in 2.0 mol L<sup>-1</sup> MSA are also tabulated in Table 9 (trials 5–7). The results show that ceric could be generated with higher current efficiency (60–70%) and the energy consumption was on the order of 0.82–1.21 kW h kg<sup>-1</sup>.

**3.3.2. Chemical Oxidation Studies.** Reaction conditions for the oxidation of *p*-methoxy-toluene to *p*-methoxy-benzaldehyde using ceric mediator was standardized by bench scale study conducted in a chemical reactor working capacity 1.0 L. Scale-up studies has been conducted using a 20 L glass reactor under the optimized condition. The reactions were conducted with continuous recycling of ceric after chemical oxidation. The obtained results are reported in Table 10. It is seen from results that the aldehyde content of crude product varied between 70–85% and the oxidant could be continuously reused without affecting the product yield and selectivity. Table 11 presents the results obtained on regeneration study of ceric. It is seen from the results that current efficiency for the regeneration would also be maintained at a constant level and the results are not affected by any organic contamination. Specific energy consumption was also nearly constant under recycling condition and the values vary between 0.9 and 1.12 kW h kg<sup>-1</sup>.

**3.3.3. Product Isolation and Characterization.** The organic layer obtained after chemical reaction was extracted using DCM solvent, and after the complete removal of aqueous layer, the organic solvent was recovered by vacuum distillation. The residues after distillation containing the product and unreacted toluene were fractionated to separate the reactant and product. GC characterized the organic residue prior to fractionation as well as the recovered reactant and pure product.

**Material Balance.** A typical material balance data for recycling trial is shown in Table 12. It is seen from the recorded data that the conversions for Ce<sup>3+</sup> to Ce<sup>4+</sup> were around 80–85% both in the first trial and regeneration. A small portion of the cerium around 5–10% gets migrated to the cathode compartment.

#### 4. Conclusions

Electrolysis conditions were standardized for the oxidation of cerous to ceric in methanesulphonic acid medium. It was observed that Ce(III) could be oxidized to Ce(IV) with the consistently higher yield over a wide range of MSA concentration. Ceric salt could also be isolated as a solid complex which can be again used for chemical oxidations. The electrochemical oxidation reaction proceeds well with platinum, DSA/O<sub>2</sub>, and TSIA anodes. Cyclic voltammetric studies present a fair indication of the oxidizability of organic compounds by ceric methanesulphonate, and this technique can be used for a rapid assessment if the viability of indirect chemical oxidation is significant. Chemical oxidation studies were conducted for the compounds *p*-methoxy-toluene gave a fairly higher yield (85%) under optimized conditions. Remarkable yield (65–78%) was achieved for the oxidation with continuous recycling while electrochemical regeneration of ceric was 70–85% with higher current efficiency. Purity of the product was also consistent during recycling. Thus it seems that indirect electrochemical oxidation for *p*-methoxy-toluene using ceric mediator is amenable for scale up as a pollution free process.

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