

ELECTROCHEMICAL OXIDATION OF Ce(III) TO Ce(IV) IN SULPHURIC ACID AND METHANE SULPHONIC ACID MEDIA - A COMPARATIVE STUDY

T VIJAYABARATHI, R KANAKAM SRINIVASAN AND M NOEL

Central Electrochemical Research Institute (CSIR), Karaikudi - 630 006, Tamil Nadu, INDIA

[Received: 22 April 1998 Accepted: 25 July 1998]

Electrochemical oxidation of cerous sulphate and cerous methane sulphonate in sulphuric acid and methane sulphonic acid were compared under various experimental conditions. The main advantage of methane sulphonic acid is the possibility of using upto 1.0 M cerous methane sulphonate with the high current density of 5.0 A/dm² compared to about 0.1 M cerous sulphate with maximum current density of around 1.0 A/dm². Lead dioxide on lead electrode could be used as anode material in sulphuric acid media. This material was not found to be effective in methane sulphonic acid media. Platinum, platinised titanium as well as TSIA anodes perform more efficiently in this media. Commercial perfluorinated cation exchange membrane is a necessary efficient separator for both media. Nafion 423 membrane was found to perform well in both the media.

Keywords: Electrochemical oxidation, cerous to ceric, methane sulphonic acid.

INTRODUCTION

Sulphuric acid has been the medium of choice for the electrochemical oxidation of Ce³⁺ salts [1]. Lead cathode and lead dioxide anode were used. Perchloric acid [2,3] and acetic acid [4] were also employed. In concentrated sulphuric acid, higher concentration of cerous sulphate could be oxidised in the slurry form in both divided [5] and undivided [6] cells. Though porous separators were employed earlier, the current trend is towards using cation exchange membranes that are stable in acid medium. The electrochemical oxidation step itself is catalysed by cobalt and silver salts [7,8]. The important limitation of sulphuric acid is the lower solubility of cerous sulphate in this media. The solubility of Ce³⁺ however is shown to increase slightly in presence of Ce⁴⁺ [9]. In recent times reports relating to use of different types of flow cells [10,11] and the dimensionally stable [12] anodes have appeared.

In the context of oxidation of methyl substituted aromatic compounds to their corresponding aldehydes higher solubility of Ce³⁺/Ce⁴⁺ redox species is a critical factor. Methane sulphonic acid [13] and trifluoromethane sulphonic acid [14] have been tried as the medium of choice during the past decade. Initially in cell oxidation in presence of cerous, ceric mediators was attempted [13]. Subsequently electrochemical oxidation of Ce³⁺ for a two stage oxidation process was reported in detail in a number of patents [14,15] and papers [16,17]. In flow cells current densities upto 20.0

A/dm² [18] and regeneration of Ce³⁺ after chemical oxidation of Naphthalene have been reported [19]. The two stage process development as a whole has also been reviewed [20,21]. Further improvements in the overall process with higher current densities and improved space time yield is being reported by another group recently [22].

As reported above the electrochemical oxidation of Ce³⁺ has been quite extensively studied in both sulphuric acid and methane sulphonic acid media. It was felt desirable to compare the electrochemical oxidation in these two important media under otherwise identical environment. This is the objective of the present investigation.

EXPERIMENTAL

A 200 ml capacity rectangular cell with catholyte and anolyte compartments separated by Nafion 423 membrane was used throughout. For comparison a few experiments were also carried out in a H-type cell to evaluate the influence of porous glass frit as separator. In sulphuric acid different anodes with working area of 0.2 dm² and a lead strip cathode of 0.02 dm² were employed. In methane sulphonic acid the anode area was 0.2 dm². Stainless steel strip within 0.25 dm² was used as cathode. L R grade cerous sulphate (Qualigens) was used as such.

Solutions of cerium methane sulphonate in methane sulphonic acid were prepared by stirring cerium carbonate (Indian Rare Earths) in water, adding concentrated methane sulphonic acid (Spectrochem. Pvt. Ltd.) both to convert

Table I: Effect of Sulphuric acid concentration

Cell: Glass cell with porous separator
 Electrodes :
 Anode : Platinum
 Cathode : Lead
 Anode c.d : 1.0 A/dm²
 Anolyte: Cerous sulphate solution containing 0.053M of Ce(III)
 Voltage : 3.0 - 3.5V

Expt. No.	H ₂ SO ₄ concn. (Molar)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	1.0	0.0319	60.19	60.2
2	2.0	0.0335	63.21	63.5
3	3.0	0.0293	55.30	55.5
4	4.0	0.0266	50.18	50.2

cerium carbonate to cerium methane sulphonate and to provide methane sulphonic acid and finally diluting with water to obtain the desired concentrations. Analysis of Ce(IV) was done by titration with ferrous ammonium sulphate using a ferroin indicator. Analysis of Ce(III) was accomplished with a silver nitrate catalyst [23] followed by Ce(IV) analysis as above.

The effect of various experimental parameters such as anode material, electrolyte concentration, Ce³⁺ concentration, anode current density on overall efficiency of electrochemical oxidation in both these media were evaluated. All the experiments were carried out at 307 ± 1 K.

RESULTS AND DISCUSSION

Electrochemical oxidation in sulphuric acid

Initially the electrochemical oxidation of Ce³⁺ was carried out in a H-type glass cell with a glass frit separator and platinum anode. Typical results showing the effect of sulphuric acid concentration on the current efficiency as well as yield efficiency are shown in Table I. Generally the current efficiency is higher upto 2.0 M sulphuric acid concentration. At higher acid concentrations yield is found to decrease slightly. The concentration of Ce³⁺ in these experiments are 0.053 moles.

Using the same H-type cell the effect of current density of platinum anode on the overall current efficiency and yield efficiency were also evaluated. In these experiments the Ce³⁺ concentration was 0.099 moles which is close to the maximum solubility of Ce³⁺ in 1.6 M sulphuric acid [23]. The current density was varied from 1.0 A/dm² to 4.0 A/dm² and the results are summarised in Table II. With increasing current density there is a systematic decrease in current efficiency as well as yield efficiency. Using the glass

Table II: Effect of current density

Cell: Glass cell with porous separator
 Electrodes : Platinum anode, Lead cathode
 Anolyte: Cerous sulphate containing 0.0991 M of Ce(III) in 1.6M sulphuric acid

Exptno.	Anode C.D (A/dm ²)	Cell voltage (Volts)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	1.0	3.0	0.0798	80.70	80.76
2	2.0	4.0	0.0760	76.90	76.95
3	3.0	5.0	0.0745	75.32	75.40
4	4.0	6.0	0.0646	65.30	65.40

frit separator the maximum current efficiency of 80% could be achieved at 1.0 A/dm². Some experiments were also carried out to evaluate the effect of separator (glass frit vs Nafion membrane 423). Electrochemical oxidation of Ce³⁺ on platinum as well as PbO₂ on Pb anode at current density namely 1.0 A/dm² and 2.0 A/dm² were carried out under identical conditions in H-type cell and membrane cell respectively. The results are summarised in Table III. This Table indicates that under all the experimental conditions investigated, membrane cells provide higher yield efficiency as well as current efficiency. In addition, migration of cerium ions to catholyte compartment is practically absent in

Table III: Effect of Separators

Electrode: Platinum anode, lead dioxide on lead anodes, Lead cathode

Anolyte: Cerous sulphate solution in 1.6M sulphuric acid

Separators: Porous separator and ion exchange membrane(Nafion 423)

Voltage: 3-4V with porous separator, 2.5-3.0V with Nafion separator

Expt. No.	Ce(III) taken (moles)	Anode	Anode C.D (A/dm ²)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	0.0990a	Platinum	1.0	0.0798	80.60	80.7
2	0.0990b	Platinum	1.0	0.0848	85.63	85.7
3	0.0990a	Platinum	2.0	0.0769	76.80	77.0
4	0.0990b	Platinum	2.0	0.0830	83.80	83.1
5	0.0577a	PbO ₂ on Pb	1.0	0.0495	85.80	85.8
6	0.0564b	PbO ₂ on Pb	1.0	0.0489	86.70	86.7
7	0.0577a	PbO ₂ on Pb	2.0	0.0450	78.00	78.4
8	0.0577b	PbO ₂ on Pb	2.0	0.0464	80.50	86.6

a = Glass cell with porous separator

b = PVC cell with Nafion separator

TABLE IV: Effect of anode materials

Cell: PVC cell with Nafion 423 separator

Anolyte: Cerous sulphate solution in 1.6 M sulphuric acid

 Anode c.d.: 1.0 A/dm²

Voltage: 2.5 - 3.0 V

Expt No	Ce(III) taken (moles)	Anode material	Anode CD (A/dm ²)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	0.0990	PbO ₂ on Pb	0.176	0.0857	86.60	87.00
2	0.0990	Platinum	0.200	0.0850	85.86	85.90
3	0.0990	Platinised titanium	0.322	0.8190	83.00	83.00
4	0.1182	Lead anode	0.198	0.0975	82.00	82.50
5	0.1731	TSIA	0.240	0.1485	85.70	85.80

membrane cells. Hence further optimization experiments were carried out using the membrane separator.

Using ion exchange membrane separator a few experiments were carried out to evaluate the effect of anode materials. Typical results obtained are summarised in Table IV. It is quite interesting to note that the current efficiency varies only in narrow range of 87.0 to 82.0 % on all the electrode materials. In the earlier literature also fairly good current efficiency have been reported on a number of electrode materials. Lead and lead dioxide anode of course would be the cheapest anode material however from pollution control viewpoint platinised titanium or TSIA anodes appear to be the electrodes of choice.

Using membrane separator and platinised titanium anodes some experiments were carried out to evaluate the effect of anode current density. A maximum current efficiency of 86.8 % was obtained at a current density of 2.0 A/dm² as

TABLE V: Effect of current densities at platinised titanium anode

Cell: PVC cell with Nafion 423 separator

Anode: Platinised titanium

Anolyte: Cerous sulphate solution containing 0.099 moles of Ce(III) in 1.6 M sulphuric acid

Expt No	Area of anode (dm ²)	Anode CD (A/dm ²)	Voltage (V)	Ce(IV) (moles)	Current efficiency (%)	Yield efficiency (%)
1	0.322	1.0	2.8-3.0	0.0819	82.7	83.0
2	0.225	2.0	3.0	0.0860	86.8	86.9
3	0.225	3.0	3.0-3.5	0.0798	80.6	80.6
4	0.225	4.0	3.5-4.0	0.0790	79.5	79.8

shown in Table V. Further increase in current density leads to lower current efficiencies.

Electrochemical oxidation in methane sulphonic acid

As mentioned above concentrated cerous methane sulphonate solutions in the range of 1.0 M may be easily prepared in methane sulphonic acid using platinum anode and stainless steel cathode at different current densities are summarised in Table VI. A current efficiency upto 90% could be achieved even at a current density of 5.0 A/dm². At higher current densities the yield efficiency as well as current efficiency drops significantly.

The effect of concentration of cerous methane sulphonate in 2.0 M methanesulphonic acid was also evaluated. These results are summarised in Table VII. Upto 1.0 M cerous methane sulphonate the yield as well as current efficiency increases with the concentration of reactant at a current density of 5.0 A/dm². Beyond this concentration level the current efficiency decreases slightly. This is apparently due to the combined effect of decreasing solubility of cerous methane sulphonate and increasing the solubility of ceric methane sulphonate with increasing concentration of methane sulphonic acid.

The effect of different anode materials for the electrochemical oxidation of cerous methane sulphonate was also evaluated as shown in Table VIII. Fairly high current efficiencies are obtained on TSIA anode, platinum and platinised titanium. Lead and lead dioxide anodes however were not found to be suitable in this medium. A white precipitate probably involving lead and methane sulphonic acid is formed on lead electrodes leading to electrode passivation.

TABLE VI: Effect of current density

Cell: PVC cell with Nafion 423 separator

Electrodes: Platinum anode, Stainless steel cathode

Anolyte: Cerous methane sulphonate of ~0.95 moles in

2.0 M methane sulphonic acid

Voltage: 2.5 - 3.9 V

Expt No	Ce(III) taken (moles)	Current density (A/dm ²)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	0.943	1.0	0.8500	90.00	90.14
2	0.935	2.0	0.8000	85.00	86.00
3	0.935	3.0	0.8072	86.30	86.50
4	0.975	4.0	0.8564	87.80	88.00
5	0.935	5.0	0.8486	90.00	90.80
6	0.975	6.0	0.7350	75.00	75.40
7	0.935	8.0	0.7060	75.40	76.00
8	0.935	10.0	0.7300	78.00	78.10

TABLE VII: Effect of Ce³⁺ concentration

Cell: PVC cell with Nafion 423 separator
 Electrodes: Platinum anode, Stainless steel cathode
 Current density: 5.0 A/dm²
 Voltage: 3.0 - 4.0 V

Expt No	Ce(III) taken (moles)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	0.2581	0.1928	71.0	74.7
2	0.4786	0.3827	80.0	80.6
3	0.7500	0.6300	84.0	84.6
4	0.9349	0.8359	89.0	89.4
5	1.2493	0.9581	76.7	77.0
6	1.3667	1.0214	75.0	77.5

The concentration of methane sulphonic acid was also found to influence the overall oxidation of cerous methane sulphonate as shown in Table IX. 2.0 M methane sulphonic acid is found to be optimum acid concentration.

CONCLUSION

The present investigations indicate the significant advantages for employing methane sulphonic acid as the medium for oxidation of Ce³⁺ ions when compared to sulphuric acid. The main advantage of methane sulphonic acid is the possibility of using up to 1.0 M cerous methane sulphonate with the high current density of 5.0 A/dm² compared to about 0.1 M cerous sulphate with maximum current density of 1.0 A/dm².

Lead dioxide on lead electrode could be used as anode material in sulphuric acid media. This material was not found to be effective in methane sulphonic acid media. Platinum, platinised titanium as well as TSIA anodes perform more efficiently in this media. Commercial perfluorinated cation exchange membrane is a necessary efficient separator for

TABLE VIII: Effect of anode materials

Cell & electrodes: Same as in Table VII
 Anolyte: Cerous methane sulphonate in 2.0 M methane sulphonic acid containing 1.062 moles of Ce(III)
 Anode current density: 5.0 A/dm²

Expt No	Anode materials	Anode area (A/dm ²)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	TSIA	0.192	0.8893	83.7	84.0
2	PbO ₂ on Pb	0.250	White precipitate formed after 20 mts of electrolysis, could not be continued further		
3	Platinum	0.200	0.9321	87.7	88.8
4	Platinised titanium	0.220	0.8929	84.08	85.0

TABLE IX: Effect of acid concentrations

Cell & electrodes: Same as in Table VII
 Anolyte: Cerous methane sulphonate,
 Anode current density: 5.0 A/dm²

Expt No	Acid concn (molar)	Ce(III) (moles)	Ce(IV) formed (moles)	Current efficiency (%)	Yield efficiency (%)
1	1.0	2.1353	1.6090	75.0	75.4
2	2.0	1.6460	1.3206	79.0	80.3
3	3.0	1.0700	0.7780	72.7	73.0

both media. Nafion 423 membrane was found to perform well in both the media.

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