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ORIGINAL PAPER

Studies on promising cell performance with H_2SO_4 as the catholyte for electrogeneration of Ag^{2+} from Ag^+ in HNO_3 anolyte in mediated electrochemical oxidation process

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Abstract Electrochemical performance of a divided cell with electrogeneration of Ag^{2+} from Ag^+ in 6 M HNO_3 anolyte has been studied with 6 M HNO_3 or 3 M H_2SO_4 as the catholyte. This work arose because in mediated electrochemical oxidation (MEO) processes with Ag(II)/Ag(I) redox mediator, HNO_3 is generally used as catholyte, which, however, produces NO_x gases in the cathode compartment. The performance of the cell with 6 M HNO_3 or 3 M H_2SO_4 as the catholyte has been compared in terms of (i) the acid concentration in the cathode compartment, (ii) the Ag^+ to Ag^{2+} conversion efficiency in the anolyte, (iii) the migration of Ag^+ from anolyte to catholyte across the membrane separator, and (iv) the cell voltage. Studies with various concentrations of H_2SO_4 catholyte have been carried-out, and the cathode surfaces have been analyzed by SEM and EDXA; similarly, the precipitated material collected in the cathode compartment at higher H_2SO_4 concentrations has been analyzed by XRD to understand the underlying processes. The various beneficial effects in using H_2SO_4 as catholyte have been presented. A simple cathode surface renewal method relatively free from Ag deposit has been suggested.

Keywords Mediated electrochemical oxidation · Ag^{2+} electrogeneration from Ag^+ · H_2SO_4 catholyte · Ag^+ migration · Ag deposit · Surface analysis · Cell performance

1 Introduction

Mediated Electrochemical Oxidation (MEO) is a well established process for ambient temperature destruction of organic waste in water [1–16]. Here a metal ion of high oxidation capacity, like, Ag^{2+} ($E^0 = 1.98$ V (NHE)), Co^{3+} ($E^0 = 1.82$ V (NHE)), Ce^{4+} ($E^0 = 1.62$ V (NHE)), Mn^{2+} ($E^0 = 1.51$ V (NHE)) etc., is utilized as a mediator to oxidize the organic compound and the reduced form of the mediator is electrogenerated in a divided/undivided cell in a closed cycle. In Ag(II)/Ag(I) based MEO system, Ag^{2+} is generated anodically from Ag^+ in an aqueous nitric acid solution (Eqs. 1–3) in a divided cell with Nafion membrane separator between the anode and the cathode [1, 2, 4–6, 8, 10]. In the cathode compartment nitric acid is reduced following the Vetter mechanism [17] to NO through nitrous acid intermediate (Eqs. 4–6) [2, 8], whose standard reduction potential is 0.957 V (NHE) [18].

At anode:

$$Ag^+ \rightarrow Ag^{2+} + e^- \quad (1)$$

$$Ag^{2+} + NO_3^- \rightarrow Ag(II)NO_3^+ \quad (2)$$

$$Ag^+ + NO_3^- \rightarrow Ag(II)NO_3^+ + e^- \quad (3)$$

At cathode:

$$HNO_3 + 2\,H^+ + 2e^- \rightarrow HNO_2 + H_2O \quad (4)$$

$$3\,HNO_2 \rightarrow HNO_3 + H_2O + 2\,NO \quad (5)$$

$$HNO_3 + 3\,H^+ + 3e^- \rightarrow NO + 2\,H_2O \quad (6)$$

The NO formation at the cathode not only leads to a continuous drop in the HNO_3 concentration in the cathode compartment, but also poses health hazardous problem.

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In the initial approach the cathodically formed NO was regenerated into nitric acid by a coupled oxidation-absorption process, which involved oxidation of NO by O_2 to NO_2 and then absorbed by water or dilute nitric acid (Eqs. 7–12) in a device consisting of an oxidation- and absorption-column at a minimal threshold pressure of 4 bar [19].

$$6\,NO + 3\,O_2 \Leftrightarrow 6\,NO_2 \tag{7}$$

$$6\,NO_2 \Leftrightarrow 3\,N_2O_4 \tag{8}$$

$$3\,N_2O_4 + H_2O \rightarrow 3\,HNO_3 + 3\,HNO_2 \tag{9}$$

$$3\,HNO_2 \rightarrow HNO_3 + 2\,NO + H_2O \tag{10}$$

$$\underline{2NO + O_2 \Leftrightarrow N_2O_4} \tag{11}$$

$$4\,NO + 2H_2O + 3O_2 \rightarrow 4\,HNO_3 \tag{12}$$

This was based on the fact that the standard reduction potential of O_2/H_2O ($E^0 = 1.22$ V (NHE)) (Eq. 13) was high enough to oxidize the nitrogen oxides directly to nitric acid (Eqs. 6, 14).

$$O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O\,(E^0 = 1.220\,\mathrm{V}\,(\mathrm{NHE})) \tag{13}$$

$$HNO_3 + 3H^+ + 3e^- \Leftrightarrow NO + 2H_2O\,(E^0 = 0.957\,\mathrm{V}\,(\mathrm{NHE})) \tag{6}$$

$$HNO_3 + H^+ + e^- \Leftrightarrow NO_2 + H_2O\,(E^0 = 0.803\,\mathrm{V}\,(\mathrm{NHE})) \tag{14}$$

Alternatively, Bringmann et al. [20] developed a simplified procedure, which worked at normal pressure, for oxidation and absorption of NO to NO_2. In this method, the nitrogen oxides mixed with a carrier gas stream of air were fed from the bottom through a thermostated bubble column, which was continuously fed with the oxidized form of a *secondary mediator* in sulphuric acid solution in a counter current mode, wherein this mediator was electroregenerated from its reduced form in the anode compartment of an another divided cell. Two mediator systems viz., Co(III)/3 M H_2SO_4 and Mn(III)/6 M H_2SO_4, were employed, since their standard reduction potentials (*vide supra*) were thermodynamically sufficient to oxidize NO_x to HNO_3 (Eqs. 6, 14). Of the two mediators, the Co(III)/3 M H_2SO_4 yielded a small conversion efficiency of 36% due to kinetic inhibition, while the Mn(III) system showed a very fast (7 to 15 s) and 97% rate of conversion of NO_x to HNO_3 at 20 °C. The recovered HNO_3 was thus free from NO_x.

Citing an example of a different approach, in which the bubble column and the second electrochemical cell for the production of *secondary mediator* were avoided, Juttner et al. [21] mentioned that investigations at Forschungsungszentrum Karlsruhe together with Eilenburger Elektrolyses-und Umweltechnik used silver containing nitric acid as anolyte and sulphuric acid as catholyte, thus avoiding NO formation at the cathode. A careful literature survey showed that systematic experimental work and details on the electrochemical cell performance with electrogeneration of Ag^{2+} in HNO_3 anolyte with H_2SO_4 as catholyte have not been reported so far.

The present work was therefore undertaken with the objective of comparing the performance of a divided cell consisting of the anodic oxidation of Ag^+ to Ag^{2+} in HNO_3 anolyte using H_2SO_4 or HNO_3 as catholyte solution. The acid concentration in the cathode compartment, the Ag^+ to Ag^{2+} conversion efficiency, the migration of Ag^+ from anolyte to catholyte, and the cell voltage have been measured during the operation of the cell over a period of time, and used for comparison. Our studies show, for the first time, that with the use of pure H_2SO_4 as a catholyte, although the NO formation in the cathode compartment is eliminated, deposition of Ag metal on the cathode occurs from Ag^+ ions crossing from anolyte to catholyte across the Nafion membrane. The intensity of Ag deposition on the electrode becomes smaller at higher concentrations of H_2SO_4; but it results in a precipitate collected in the solution. The composition of the precipitate and the surface composition of the cathode have been analyzed using XRD, SEM and EDXA techniques to unravel the underlying processes. A simple method to renew the cathode surface relatively free from Ag deposits has also been demonstrated.

2 Experimental

2.1 Materials

Silver(I) nitrate (99.8%) from Junsei Chemical Co. Ltd., Japan, nitric acid (60%) from Sam Chun Chemicals, Korea, and sulphuric acid (95%) from DC Chemicals Co Ltd, Korea were used as-received. Mesh-type Pt-coated-Ti and Ti electrodes were purchased from Wesco, Korea. Nafion® 324 membrane was from Dupont, USA. All the solutions were made using water purified by reverse osmosis (Human Power III plus, Korea).

2.2 Apparatus

Figure 1 shows the schematic diagram of the Ag(II) electrochemical generation process. A flow type electrochemical reactor consisting of anode and cathode compartments separated by a proton conducting Nafion® 324 membrane of thickness 0.15 mm was used. The membrane is capable of allowing protons from anodic to cathodic compartment to maintain the current flow. Mesh type Pt-coated-Ti and Ti

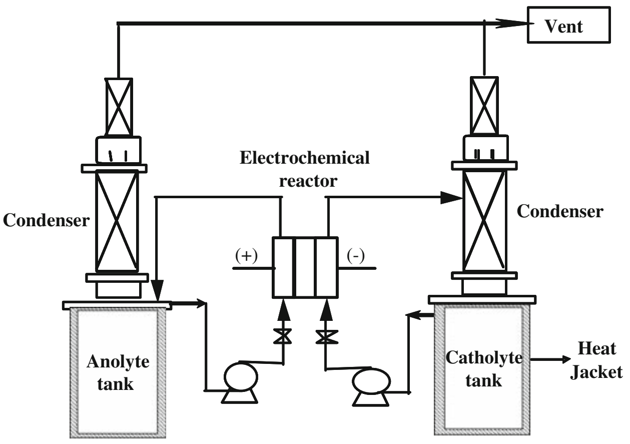


Fig. 1 Schematic diagram of the electrochemical reactor

electrodes with a geometrical area of 140 cm^2 (10 cm × 14 cm × 0.5 cm) were used as the anode and the cathode, respectively. The effective surface area of the electrodes was 112 cm^2.

A 500 mL solution of 0.1 M Ag(I) in 6.0 M nitric acid and an equivalent volume of 3.0 M sulphuric acid (or 6.0 M nitric acid) were taken in separate anolyte and catholyte glass reservoirs, respectively. The electrolyte solutions were continuously circulated through the anode and cathode compartments of the electrochemical cell at a constant flow rate. The temperature in both the anolyte and the catholyte reservoirs was maintained constant at a pre-set value by water circulation through the double-walled jacket provided for the reservoirs. Constant-current electrolyses were performed by a locally made constant current source from Korea Switching Instrument.

All the measurements were conducted at 24 ± 1 °C, with an electrolysis current of 10 A and a constant flow rate of 2.5 $dm^3\ min^{-1}$.

2.3 Analytical procedure

The concentration of Ag(II) in analyte solution at any time t, $[c_{Ag(II)}]_{A,t}$ was determined by stoichiometric oxidation of Ce(III) to Ce(IV) by Ag(II) followed by titrating Ce(IV) against standard Fe(II) solution by potentiometric method. The Ag(I) to Ag(II) conversion efficiency at time, t, was calculated as $[c_{Ag(II)}]_{A,t}/[c_{Ag(I)}]_{Initial}$, where $[c_{Ag(I)}]_{Initial}$ was the initial Ag(I) concentration.

To estimate the total silver ion concentration in the anolyte at a given time, the anolyte containing the Ag(I) and Ag(II) mixture was treated with Fe(II), which reduces Ag(II) to Ag(I); and the total Ag(I) was then titrated against standard KCNS solution.

The H_2SO_4 (or HNO_3) concentration in the catholyte was estimated by the usual titration method.

2.4 SEM, EDXA and XRD measurements

The surface morphology of the cathode was investigated by a JEOL-JSM 5700F scanning electron microscope coupled with microprobe analysis (energy dispersive X-ray analysis). The microscope was operated at 20 kV. The X-ray powder diffraction measurement on the precipitate samples collected from the cathode compartment was performed on a Dmax-2500 IPC X-ray diffractrometer (RIGAKU Co. Ltd., Japan) with Cu K_α radiation and graphite monochromator.

3 Experimental results

3.1 Electrochemical studies with HNO_3 versus H_2SO_4 as catholyte

To compare the effect of HNO_3 and H_2SO_4 as catholyte, the performance of the electrochemical divided cell was studied with 0.1 M Ag(I) in 6 M HNO_3 anolyte using 6 M HNO_3 or 3 M H_2SO_4 as a catholyte, and results are shown in Figs. 2 and 3. With 6 M HNO_3 as catholyte the HNO_3 concentration in the cathode compartment decreases quite considerably during electrolysis from 6.0 to 4.9 M in 240

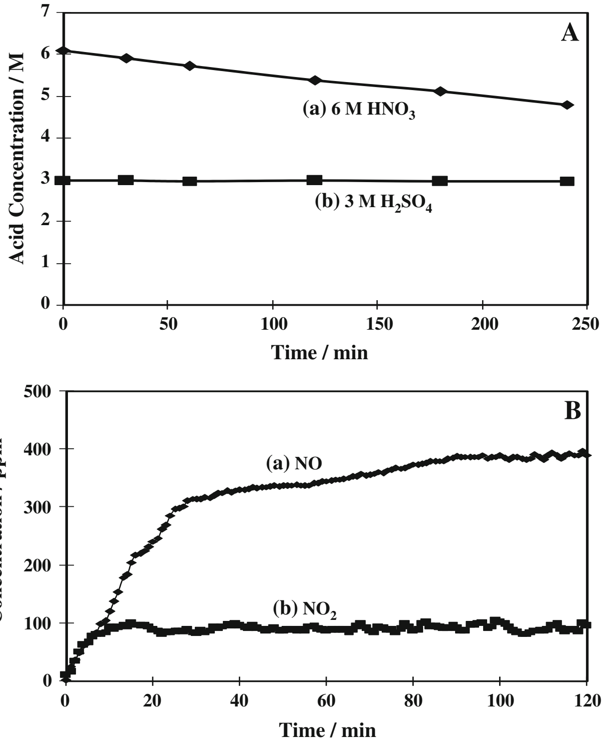


Fig. 2 (**A**) Variation of acid concentration in the cathode compartment versus electrolysis time for (a) 6 M HNO_3; (b) 3 M H_2SO_4. (**B**) Concentration of NO_X gases evolved from cathode compartment with 6 M HNO_3 catholyte: (a) NO; (b) NO_2 (Experimental conditions: anolyte = 6 M HNO_3 containing 0.1 M $AgNO_3$, applied current = 10 A, anolyte and catholyte flow rate = 2.5 $dm^3\ min^{-1}$)

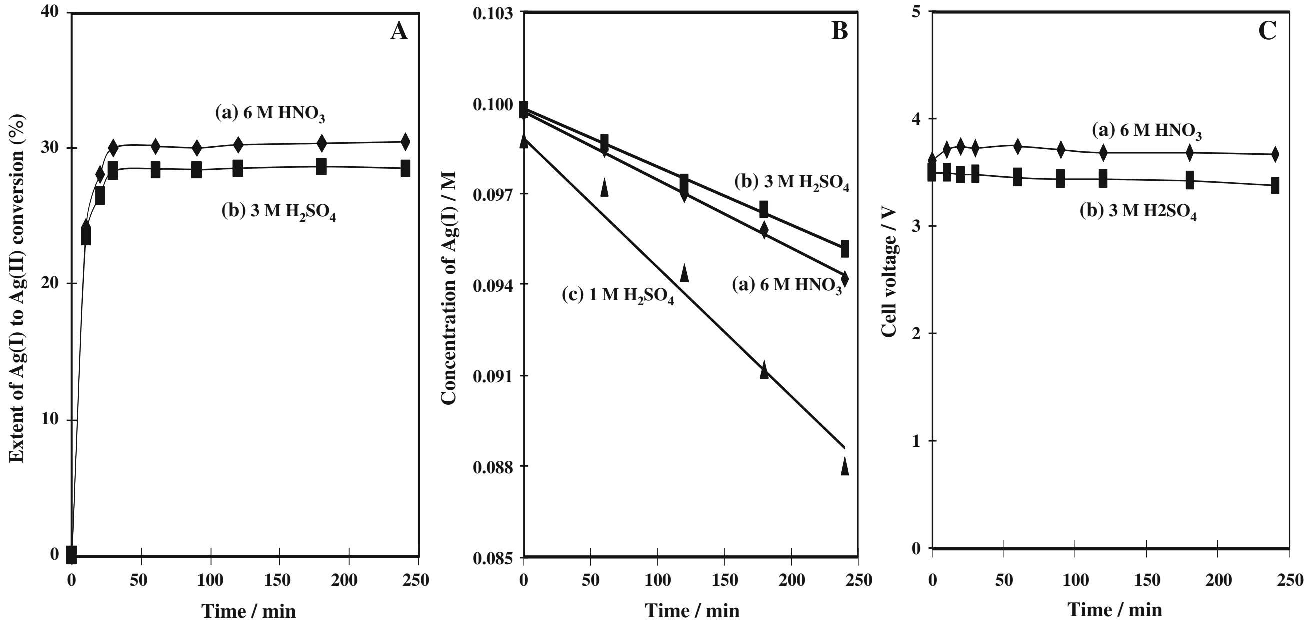


Fig. 3 Variation of (**A**) extent of Ag(I) to Ag(II) conversion (%) in anolyte, (**B**) total Ag(I) concentration in anolyte, (**C**) cell voltage, as a function of electrolysis time for different catholytes: (a) 6 M HNO_3; (b) 3 M H_2SO_4. Curve (c) in (**B**) represents total Ag(I) concentration in anolyte when 1 M H_2SO_4 was used as catholyte (Experimental conditions: anolyte = 6 M HNO_3 containing 0.1 M $AgNO_3$; applied current = 10 A; anolyte and catholyte flow rate = 2.5 dm^3 min^{-1})

min as shown in Fig. 2A. This is apparently because the cell reaction involves the anodic oxidation of Ag(I) to $Ag(II)NO_3^+$ (Eqs. 1–3), and the cathodic reduction of HNO_3 to NO and NO_2, as described in Eqs. 4–6. The quantities of NO and NO_2 from the off-gas stream emanated from the cathode compartment was estimated using a Teledyne Gas Analyser Instrument Model No. 9560 and the results are shown in Fig. 2B. The steady-state concentrations of NO and NO_2 are found to be around 11,400 ppm and 2,700 ppm, respectively, per liter of air.

Unlike HNO_3, the H_2SO_4 acid as the catholyte remains unaltered in concentration over the entire experimental period (Fig. 2A, curve b), since the SO_4^{2-} anion cannot be reduced at the cathode and the cathodic reaction in this case is the reduction of hydrogen ions (Eq. 15), migrated from anolyte to catholyte through the Nafion membrane.

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \qquad (15)$$

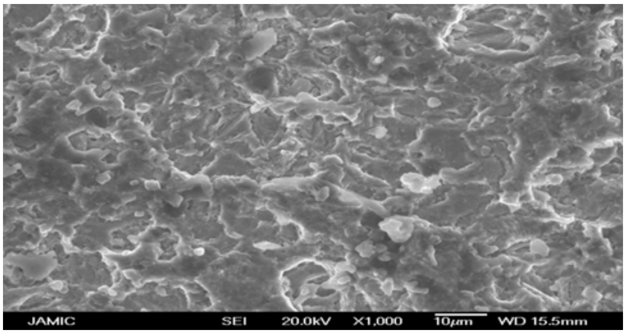
In Fig. 3, the other experimental results for H_2SO_4 or HNO_3 as the catholyte are compared: the extent of Ag(I) to Ag(II) conversion (%) in the anolyte (Fig. 3A), the total silver ion concentration as Ag(I) in the anolyte (Fig. 3B) and the cell voltage (Fig. 3C). The amount of Ag(II) produced at the anode is slightly lower when H_2SO_4 was used as the catholyte, Fig. 3A. On the other hand, the migration of Ag(I) from anolyte to catholyte occurs to a somewhat lesser extent (Fig. 3B) and the cell voltage is also slightly smaller (Fig. 3C) for H_2SO_4 as the catholyte.

3.2 SEM, EDXA and XRD studies for H_2SO_4 catholyte system

It is well known that in Ag^{2+}/Ag^+ based MEO systems with HNO_3 as the catholyte, silver deposition occurs at the cathode in preference to direct HNO_3 reduction (Eqs. 3–6) at low HNO_3 concentrations. Thus, higher concentrations of HNO_3 are used in order to avoid the Ag deposition problem [1, 2, 4–6]. In order to verify which is the preferred cathodic reaction in the case of H_2SO_4 catholyte, whether Ag deposition or H^+ reduction (Eq. 15), and the dependence of this behavior on the acid concentration, the morphology of the cathode surface was analyzed for Ag by SEM and EDAX after electrolysis was carried-out with different concentrations of H_2SO_4 (1 and 3 M). In all these experiments, the anolyte 6 was M HNO_3 containing 0.1 M silver. The current and flow rate were kept at 10 A and 2.5 dm^3 min^{-1}, respectively, and the duration of electrolysis was 240 min. For comparison unexposed Ti samples were also analyzed for SEM and EDXA.

The results for unexposed the Ti sample are shown in Fig. 4. The Scanning electron micrograph, Fig. 4**a,** exhibits a highly flaky, rough and porous surface typical of an oxidized layer [22]. The entire area was analyzed at three locations by EDXA and all of them show stronger peaks of Ti and O and minor peaks of Fe, S and Na, as shown in Fig. 4b. The percentage analyses of different particles are listed in the figure. The results suggest that the Ti surface is oxidized. While the

a SEM



b EDXA

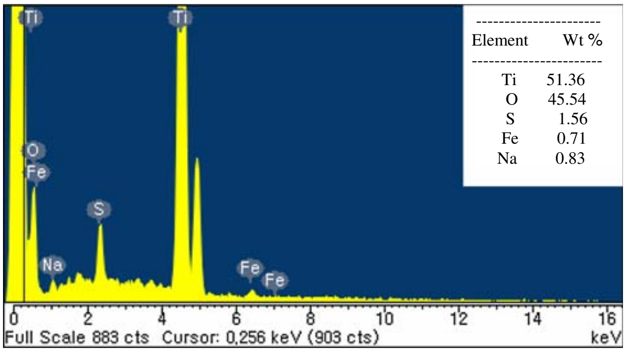


Fig. 4 (**a**) SEM image and (**b**) EDXA spectrum of unexposed Ti cathode sample

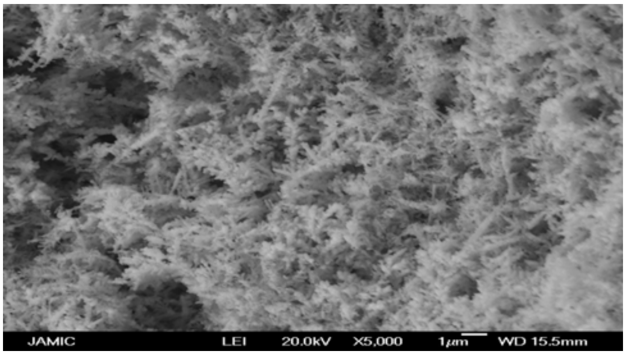
source for S is likely the electrolyte H_2SO_4, the Fe and Na may be associated with the Ti electrode material.

Figure 5a shows an SEM image of deposited silver on Ti cathode when 1 M H_2SO_4 was used as catholyte. Leaf-shaped dendrites of silver can be seen, the presence of which is further confirmed by stronger peaks of silver in the EDXA analysis (Fig. 5b). The EDXA peaks for Ti, Fe, Na and O are completely absent, indicating that the silver is deposited throughout the Ti surface. The SEM image shows that the dendrites are more branched off in all directions and dense. The catholyte gave a positive test for the presence of Ag^+ ion at the end of electrolysis for 240 min in the divided cell, when tested with KCl. This suggests that Ag^+ ions are present in H_2SO_4 solution as silver sulfate (Ag_2SO_4), which is fully dissociated into Ag^+ and $SO_4{}^{2-}$ ions (Eq. 16). The solubility product of Ag_2SO_4 is 1.2×10^{-5} M^3 [23].

$$Ag_2SO_4 \Leftrightarrow 2Ag^+ + SO_4{}^{2-} \qquad (16)$$

When 3 M H_2SO_4 was used as the catholyte, the surface analyses (Fig. 6) as well as solution result showed different behavior. The SEM pictures, Fig. 6a at ×1000 magnification and Fig. 6b at ×300 magnification, show that only some parts of the Ti surface are covered with big-sized silver globules. The appearance of some free dendrites on silver globules can be seen. The majority of the Ti cathode area is completely free from any form of silver deposit. EDXA results also confirm this behavior e.g., at the location marked #2 in SEM picture (Fig. 6b), no peak for silver is observed in the EDXA recorded at this point, Fig. 6d. The 3 M H_2SO_4 system also gave the following additional information. At the end of electrolysis for 240 min in the divided cell, a dense grey-colored precipitate was collected at the bottom in the cathode compartment. Besides, both the catholyte solution and the precipitate at the end of electrolysis gave a negative test for Ag^+ ions when tested with KCl solution indicating that no free Ag^+ ions are present in 3 M H_2SO_4 catholyte solution. The solution behavior of 3 M H_2SO_4 is different from that of 1 M H_2SO_4 which showed a huge amount of free Ag^+ ions in solution and which has been interpreted in terms of Ag_2SO_4 in solution completely dissociated into Ag^+ and $SO_4{}^{2-}$ ions (Eq. 16). Thus, the solid observed in 3 M H_2SO_4 is probably precipitated Ag_2SO_4 since, according to the well known "common ion effect", increase in $SO_4{}^{2-}$ ion concentration could lead to a decrease of the solubility of silver sulfate [24]. Following this, the precipitate in 3 M H_2SO_4 was examined by XRD measurements to determine the nature of the product and its authenticity. The XRD patterns of the precipitate sample are presented in Fig. 7.

a SEM



b EDXA

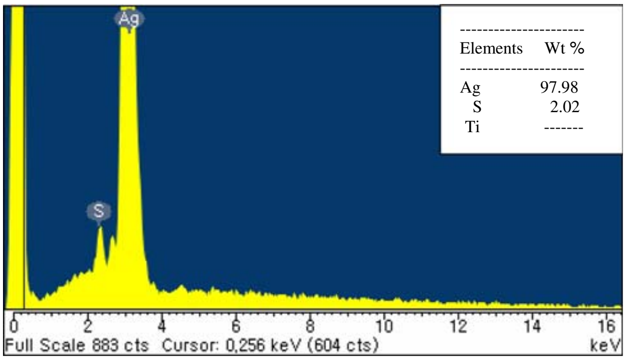
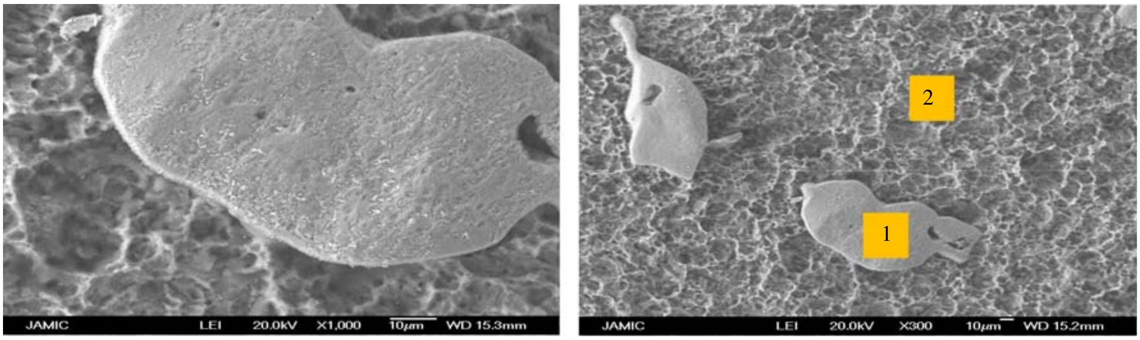
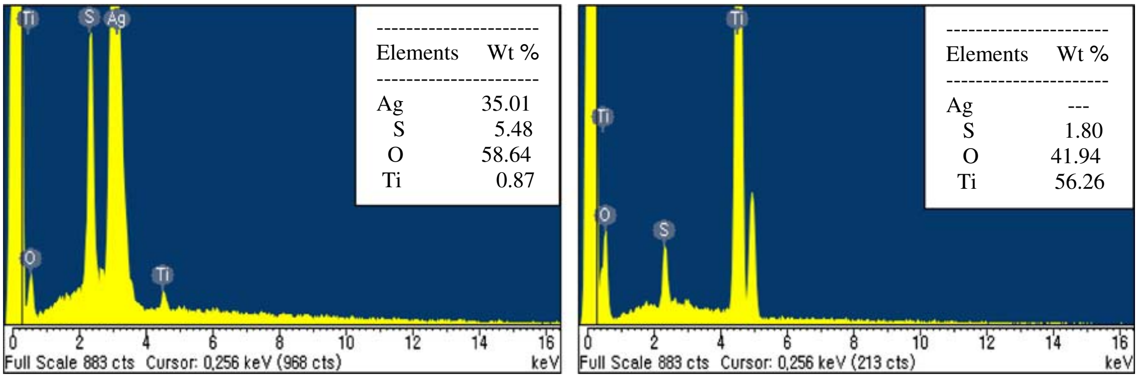


Fig. 5 (**a**) SEM image and (**b**) EDXA spectrum of the Ti cathode surface with silver formed in 1 M H_2SO_4 catholyte (Anolyte = 6 M HNO_3 containing 0.1 M $AgNO_3$, current = 10 A, flow rate = 2.5 dm^3 min^{-1})



a SEM (X 1000)

b SEM (X 300)



c EDXA at location # 1

Elements	Wt %
Ag	35.01
S	5.48
O	58.64
Ti	0.87

d EDXA at location # 2

Elements	Wt %
Ag	---
S	1.80
O	41.94
Ti	56.26

Fig. 6 SEM images and EDXA spectra of the Ti cathode surface with silver formed in 3 M H_2SO_4 catholyte: (**a**) SEM (×1000); (**b**) SEM (×300); (**c**) EDXA at location # 1; (**d**) EDXA at location #2 (Anolyte = 6 M HNO_3 containing 0.1 M $AgNO_3$, current = 10 A, flow rate = 2.5 dm^3 min^{-1})

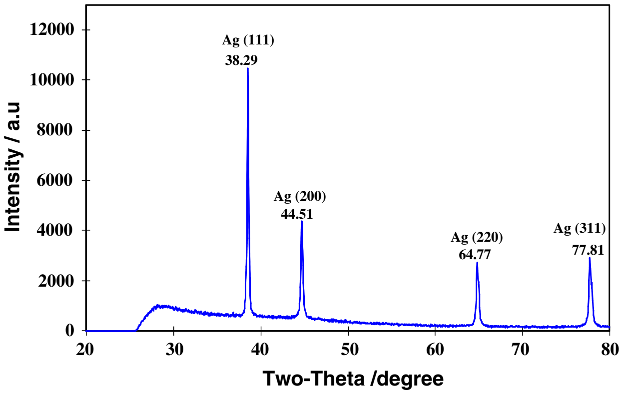


Fig. 7 XRD spectrum of the precipitate collected in 3 M H_2SO_4 catholyte compartment

The spectrum exhibits very strong peaks of Ag metal (JCPDS File No.01-071-4612), which confirms that the collected solid material in 3 M H_2SO_4 catholyte solution is not silver sulfate but pure silver metal, and the adhesion of deposited silver on Ti cathode is very weak in concentrated sulfuric acid solution. The XRD results corroborate our earlier finding of negative test for Ag^+ ions in the precipitate and in solution.

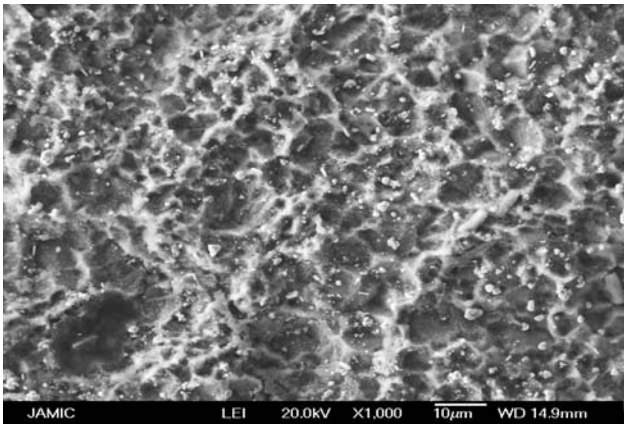


Fig. 8 SEM image of the Ti cathode surface with silver formed in 3 M H_2SO_4 catholyte (Fig.6a) after washings by circulating 3 M H_2SO_4 repeatedly

Some tests were conducted to renew the Ti cathode surface after the experiments in 3 M H_2SO_4. It was observed that the big silver globules on the Ti cathode (ca. Fig. 6a at ×1000 magnification) could be very easily dislodged from the surface by circulating 3 M H_2SO_4 repeatedly. Figure 8 (at ×1000 magnification) shows the SEM image of a Ti surface subjected to the above treatment. Few tiny Ag crystals (confirmed by EDXA, not shown) are present on some parts of the surface. Comparison of Figs. 6a and 8 indicates that the tiny Ag crystals on the surface are only a small fraction disintegrated from the big silver globules. Most of the silver material settles as precipitate at the bottom of the solution.

4 Discussion

The cell performance results collected in Figs. 2 and 3, for electrooxidation of Ag^+ to Ag^{2+} in 6 M HNO_3 anolyte with HNO_3 or H_2SO_4 at the same proton concentration (6 M) as catholyte, clearly reveal that there are several advantages in using H_2SO_4 as the catholyte in the divided cell. For example, the H_2SO_4 concentration remains the same throughout the electrolysis duration (Fig. 2A, curve b), and also there is a lesser migration of Ag^+ ion from anolyte to catholyte across the Nafion membrane separator (Fig. 3B, curve b). Moreover, the voltage that develops across the cell is also slightly smaller in this case (Fig. 3C, curve b). Looking at the reasons for such a favorable behavior of the H_2SO_4 system, it is easy to understand the constant concentration of H_2SO_4 in the catholyte during electrolysis, since H_2SO_4 is not directly reduced at the cathode, but it is only the hydrogen ions, migrating from anolyte to catholyte through the Nafion membrane, that are reduced as in Eq. 15; whereas, in the case of HNO_3, it is directly reduced at the cathode generating poisonous NO_x gases as in Eqs. 4 to 6. Coming to the lesser migration of Ag^+ ions from 6 M HNO_3 anolyte into 3 M H_2SO_4 catholyte, than into 6 M HNO_3 catholyte, the low solubility of metal ions in sulfuric acid [10] might be responsible for the reduced Ag^+ migration into this acid. The low cell voltage for H_2SO_4 catholyte is an indication that the internal resistance in the cell circuit is smaller for this system.

Studies with various concentrations of H_2SO_4 catholyte coupled with surface morphology of the cathode by SEM and EDXA indicate that the acid concentration has a great impact both on the morphology of silver deposit and the solution behavior. In the case of 1 M H_2SO_4, silver was deposited on the Ti surface uniformly as dendrites (Fig. 5), and the catholyte solution at the end of the electrolysis contained free Ag^+ ions. In contrast, the silver deposits on the cathode surface adhere poorly in the case of 3 M H_2SO_4 (Fig. 6) with the result that solid Ag metal was collected in solution as dense grey precipitate (Fig. 7). Also, there was no dissolved form of silver ion observed in 3 M H_2SO_4 solution.

The higher quantities of free Ag^+ ions in 1 M H_2SO_4 catholyte are closely related to the greater migration of Ag^+ ions from anode to cathode compartment across the anionic Nafion membrane separator, as shown in Fig. 3B curve c. The faster drop in the Ag^+ ion concentration in the anode compartment for 1 M H_2SO_4 catholyte compared to 3 M H_2SO_4 catholyte (Fig. 3B, curves b) is reasonable since the potential drop that develops across the membrane, which is the additional driving force for ionic migration, is higher with 6 M HNO_3 on one side and 1 M H_2SO_4 on the other side of the membrane compared to when 1 M H_2SO_4 is replaced by 3 M H_2SO_4.

Thus, with smaller quantities of migrated Ag^+ ions in 3 M H_2SO_4 catholyte, there appears to be complete reduction to silver metal in this case, as evidenced from the absence of free Ag^+ ions in the solution. The poor adhesion of the silver deposit on Ti in 3 M H_2SO_4 solution may arise for the following reason. The Ti electrode surface used in the present work is heavily oxidized, as shown by EDXA (Fig. 4b). There are reports that the outermost surface of an oxide film is covered by layer of hydroxyl groups forming hydroxylated species in aqueous solutions [25, 26]. Therefore, a variation in electrode surface charge with acid concentration leading to a change in its interaction with the hydrated silver deposit may be responsible for the difference in adhesion behavior, although the exact mechanism is difficult to be envisaged. However, it is important to quote a recent study on silver deposition on copper electrode, which reported H_2SO_4 electrolyte concentration-dependent adherence of the silver deposit formed in the cementation process conducted in deoxygenated conditions [27].

The absence of any Ag^+ ions in solution due to complete reduction, and the solid Ag metal collection in the solution due to poor deposit-adherence on the cathode surface in H_2SO_4 catholyte solution of high concentration provide considerable promise compared to the conventional HNO_3 system. Generally, the recovery of silver from the process stream of Ag(II)/Ag(I) based MEO system with HNO_3 as a catholyte requires an additional electrodeposition stage, which can be totally avoided in H_2SO_4 catholyte based system, since the solid Ag can be directly recovered in the cathode compartment. Further to this, our studies have shown that the collection of solid Ag metal can be further enhanced by repeated electrode washings with catholyte circulation.

Thus, from a comparative cell performance studies with H_2SO_4 or HNO_3 as the catholyte, and from surface morphology studies of cathode by SEM and EDXA for H_2SO_4 acid of different concentrations, several environmental (no NO_x liberation) and economical (low cell voltage and no additional silver recovery stage) benefits in using H_2SO_4, particularly high concentrations, should have become obvious. It should, however, be mentioned that there are several fundamental issues; for example, a more appropriate explanation for lesser migration of Ag^+ ions and smaller cell voltage in the case of H_2SO_4, compared to

HNO_3, requires additional experiments to obtain exact parameters, like, potential across the Nafion membrane with 6 M HNO_3 (containing $AgNO_3$) on one side and 6 M HNO_3 or 3 M H_2SO_4 on the other side, its dependence on solution activity, the electrode kinetic data for the individual anodic and cathodic reactions of both HNO_3 and H_2SO_4 catholyte systems at the respective electrodes (Pt-coated-Ti anode and Ti cathode), etc. Knowing these parameters should be interesting in order to verify the above observations, but also to optimize some process parameters for better utilization of the newly identified H_2SO_4 catholyte system.

5 Conclusion

For Ag^+ oxidation to Ag^{2+} in HNO_3 anolyte in a divided cell the use of H_2SO_4 as catholyte, instead of the customarily used HNO_3, offers several beneficial effects in the cell performance: (i) the catholyte remains unaltered in concentration over the entire experimental period, (ii) the migration of Ag^+ ion from anolyte to catholyte across the Nafion membrane separator is smaller, (iii) the cell voltage is also slightly smaller. Studies with various concentrations of H_2SO_4 catholyte coupled with surface morphology of cathode by SEM and EDXA indicate that the acid concentration has a great impact on the morphology of silver deposit. At lower H_2SO_4 concentration (1 M), leaf-shaped dendrites of silver are deposited uniformly on the cathode. At higher concentrations like 3 M, instead of uniform deposition, relatively big-sized globules spread scarcely on the surface appear, along with sizable portion of solid precipitate, identified as silver metal by XRD, collect at the bottom. Moreover, the big globules on the cathode surface can be easily dislodged and collected in the cathode compartment simply by repeatedly circulating the catholyte solution. This last observation is particularly promising since silver recovery can be directly achieved in H_2SO_4 catholyte based system, thus avoiding the additional electrodeposition stage associated with the customarily used HNO_3 catholyte. Because of the several attractive attributes of the "Ag(II)/Ag(I) in HNO_3 anolyte and H_2SO_4 catholyte–based-MEO system", it is being applied for the oxidative degradation of NO_x, SO_x and othor gases at present and the results will be communicated elsewhere in the near future.

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