

Selenate ion Reduction on Titanium oxide Electrode Synthesized by Electrooxidation of Titanium Metal.

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A selenate ion in aqueous solution can be reduced by electrolysis on a titanium oxide cathode, which is made by an electro-oxidation of a titanium metal plate in a nitric acid solution. The selenate ion is reduced to amorphous selenium with the current efficiency more than 50 % when the selenate concentration is 50 ppm as selenium and the current density is $0.33 \text{ mA}\cdot\text{cm}^{-2}$. The current efficiency decreases with the selenate concentration becoming low. However, the current efficiency is larger than 20 % when the selenium concentration is under 2 ppm, and the selenium concentration can be decreased under 0.1 ppm.

Key words: Selenate, Electro reduction, Titanium oxide electrode

1. INTRODUCTION

Selenium is contained in sulfide ore and coal. Therefore, the wastewater from smelters those treat sulfide ore and coal burning power plants contains selenium. Selenium in the wastewater exists mainly as a selenite (SeO_3^{2-}), but some selenium exists as a selenate (SeO_4^{2-}). A selenate ion is very stable in an aqueous solution because it has the same structure as sulfate ion, and it needs sever conditions to reduce it [1, 2].

We found that the selenate is smoothly reduced by titanium dioxide photocatalyst [3]. This indicates that the electron transfer from a titanium dioxide surface to a selenium in the selenate ion, can proceed smoothly, and this suggests the selenate ion can be reduced also the electrolysis on the titanium dioxide electrode. The titanium dioxide cannot be used as anode without irradiation because it is an n-type semiconductor, but it can be used as cathode. We tried to reduce selenate ion by electrolysis with a titanium dioxide cathode which is coated on the tin oxide coated glass by spray pyrolysis method, and found that the selenate ion can be reduced on those cathode [4, 5].

It needs large area titanium oxide electrodes that have no pinhole and no clack, to remove selenium from the wastewater efficiently. If there are some holes or cracks in the titanium oxide film of the electrode, substrate contacts with the solution, and hydrogen evolution proceeds there. This decreases the current efficiency largely. Titanium dioxide film made by spray pyrolysis has high activity as photocatalyst or photo electrode, but it is difficult to get large area.

The titanium oxide electrode made by the electro-oxidation of the titanium metal is thought to satisfy the above-mentioned requirement.

We report about the reduction reaction of selenate ion in aqueous solution on the titanium oxide electrode made by the electro-oxidation of titanium metal substrate.

2. EXPERIMENTS

2.1 Electrode fabrication

Titanium oxide electrode is fabricated from a titanium metal plate, which is common grade and 0.2

mm thick. This is cut into $3\sim 10\text{cm}\times 10 \text{ cm}$, and is immersed into 8 or 13 vol. % Nitric acid, then it is electro-oxidized with the HZ-3000 potentiostat (Hokuto Denko). A platinum plate electrode and an Ag/AgCl electrode are used as the counter electrode and the reference electrode, respectively. The electrolysis is carried out under a potentiostatic condition without any temperature control. The electrode potential is +5.0 V vs. Ag/AgCl or + 8.0 V vs. Ag/AgCl, and electrolysis time is 0.5, 1 or 2 hours. After the electrolysis, the electrode is rinsed with ion exchange water, and dried in air at room temperature.

The fabricated electrode is analyzed with X-ray diffract meter (RINT 2500, Rigaku Denki).

2.2 Selenate reduction

Sodium selenate solution is used as a model wastewater, and 2.5 mol/l formic acid or 2.5 mol/l sulfuric acid is added to control the pH. A Tall beaker (100 ml) is used as the electrolysis cell. 100ml of model wastewater is put into the cell and 1 ml of acid solution is added to it. The titanium oxide electrode, the Pt plate electrode and the Ag/AgCl electrode are immersed into the cell, and also a glass tube is immersed. The electrolysis is carried out under a galvanostatic condition without any temperature control. During electrolysis, the model wastewater is stirred with a magnetic stirrer and N_2 gas is bubbled via the glass tube.

After the electrolysis, the model wastewater is filtrated by a filter paper (for quantitative analysis, No. 5C, ADVANTEC) or a syringe filter (pore size is $0.2 \mu\text{m}$, ADVANTEC DIMIC-25). The filtrate is analyzed by the ICP (Seiko Instruments SPS3000) and the remaining selenium concentration is determined.

The electrodes are immersed into conc. Nitric acid at room temperature for several tens minutes to remove the amorphous selenium from their surface, and they are reused.

3. RESULTS AND DISCUSSION

3.1 Electrode fabrications and their structure

The current decreases with time during the electro-oxidation of a titanium metal substrate

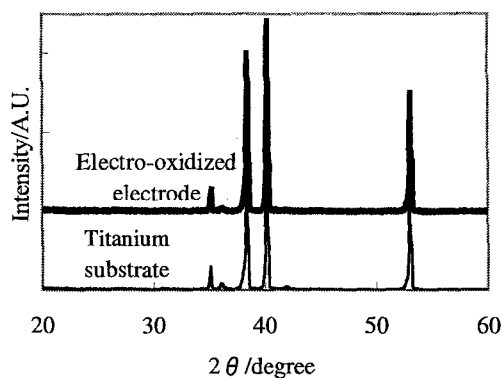


Fig. 1 XRD pattern of the titanium metal substrate and the electro-oxidized electrode. Cu-K α line is used, and the X-ray power is 40 kV- 200mA.

under a potentiostatic condition. This is because the thickness of the oxide layer increases with the progress of the electrolysis. After the electro-oxidation, the color of the titanium substrate surface becomes yellow or gold.

Fig. 1 shows the XRD pattern and fig. 2 shows the potential-current curve in the aqueous solution containing 6.33×10^{-4} mol/l of Na_2SO_4 and 25 mmol/l of formic acid, of the electro-oxidized titanium oxide electrode which was oxidized for 2 hr under 5.0 V vs. Ag/AgCl. Large cathodic current is observed, but anodic current is very small. This indicates that the electrode surface becomes n-type semiconductor, in the other words, the titanium dioxide layer is formed on the titanium metal surface. On the contrary, there are little difference in the XRD pattern between the titanium metal and the electro-oxidized titanium oxide electrode. These results show the titanium oxide, which is formed at the surface of the titanium metal substrate, is amorphous or microcrystalline or very thin, and this is because the oxidation is carried out at room temperature and relatively low electrode potential.

3.2 Selenate reduction

The electrodes made by the electro-oxidation of titanium metal, have activity to reduce the selenate ion. Fig. 3 shows the potential change during the electro-reduction reaction. There is a tendency of the potential shifting toward to minus direction, but the change is not large. Small particles of amorphous selenium are generated in the solution during electrolysis. These particles can be separated from the solution by filtering with the syringe filter or the filter paper.

The reduction reaction of selenate ion to amorphous selenium is written as follow.

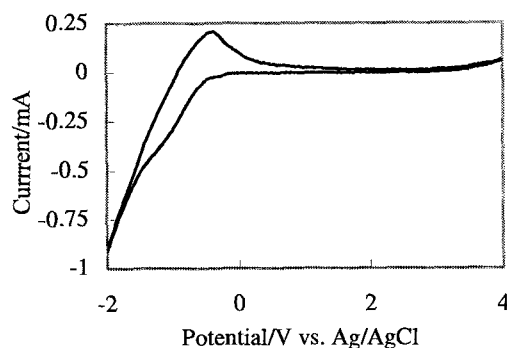
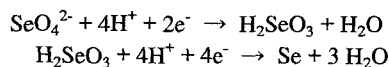


Fig. 2 Current-Potential curve of electro-oxidized titanium oxide electrode, in 6.33×10^{-4} mol/l of Na_2SO_4 aqueous solution containing 25 mmol/l of formic acid.

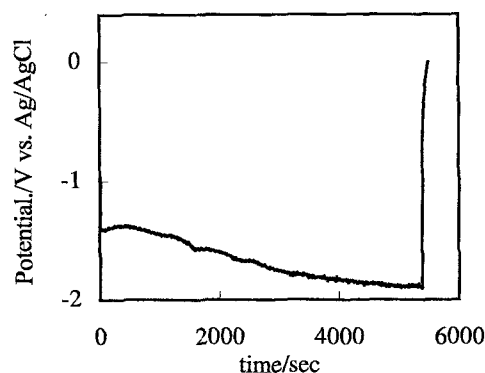


Fig. 3 Potential change during the electro-reduction reaction of selenate ion. Initial selenium concentration is 10 ppm and current density is $0.167 \text{ mA} \cdot \text{cm}^{-2}$.

It needs 6 electrons to reduce selenate ion to amorphous selenium. The current efficiency, Eff is calculated as follows.

$$Eff = \left(\frac{\Delta C \times V}{M_{Se}} \times 6 \times F \right) \div Q \times 100$$

Where ΔC , V , F , M_{Se} and Q are the difference between the initial and the remaining selenium concentration, the volume of the model wastewater, the atomic weight of selenium, the Faraday constant and the quantity of electricity flowed during the electrolysis, respectively.

Fig. 4 shows the relations among the electrode fabrication condition, current density of the selenate reduction electrolysis and current efficiency when the initial selenium concentration is 50 ppm. There are large scatters, but we think that there is little difference among the activities of the electrodes, which are electro-oxidized under different conditions. Oxide layer, which has a sufficient activity for selenium reduction, seems to be formed on the substrate surface

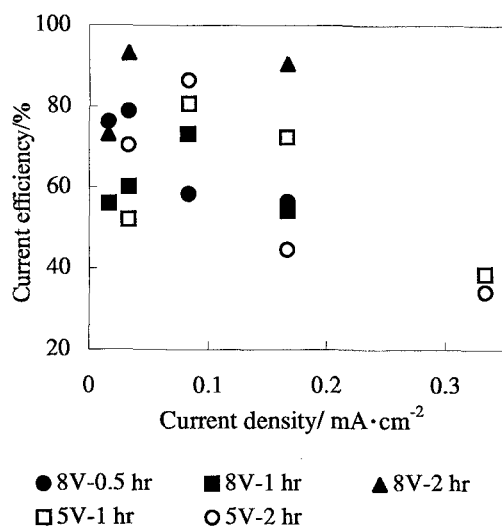


Fig. 3 The current efficiencies when the initial selenium concentration is 50 ppm, and 2.5 mmol/l of sulfuric acid is added. Electrode surface area is 30 cm² for oxidized under 5V vs. Ag/AgCl, and 60 cm² for oxidized under 8 V vs. Ag/AgCl.

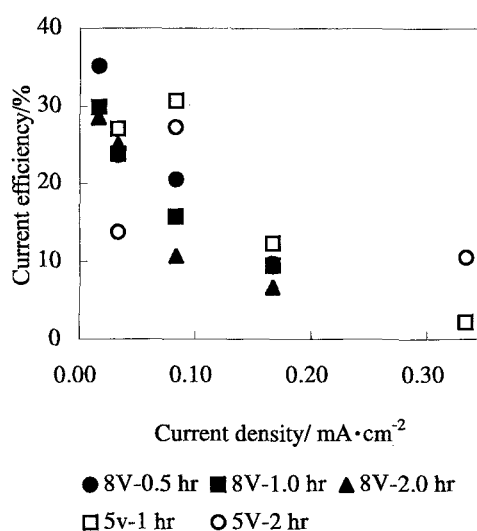


Fig. 4 The current efficiencies when the initial selenium concentration is 10 ppm. The other conditions are same as fig. 3.

under these electro-oxidation conditions.

There is the tendency that current efficiency increases with the current density decreasing. This is reasonable because the diffusion rate is decided by the selenate concentration and stirring condition, which are kept at constant. Therefore, the diffusion rate is almost constant and the selenate ion moves to the electrode surface only by diffusion in this reaction.

Fig. 5 shows the relation between the current density and the current efficiency, when the initial selenium concentration is 10 ppm. The current efficiency is smaller, than that when the initial selenium concentration is 50 ppm, but the tendency is similar.

Table I The current efficiency when the initial Se concentration is 2 ppm

Current density /mA·cm ⁻²	Remaining Se concentration/ppm	Current efficiency
0.17	1.495	12%
	1.401	15%
	1.483	13%
0.033	0.816	48%
	1.002	41%
	0.879	46%

2.5 mmol/l of formic acid is added, with the electrode, oxidized 2 hr at 5 V vs. Ag/AgC, and its surface area is 30 cm².

Table II The current efficiency and remaining Se concentration when the initial Se concentration is 2 ppm.

Remaining Se concentration/ppm	Current efficiency	1st step		2 nd step		3ed step	
		Current density /mA/cm ²	Time/min	Current density /mA/cm ²	Time/min	Current density /mA/cm ²	Time/min
0.28	35%	0.02	30	-	-	-	-
0.18	37%	0.01	30	0.005	60	-	-
0.15	38%	0.02	15	0.01	30	-	-
0.022	20%	0.02	30	0.01	60	-	-
0.043	27%	0.02	15	0.01	60	-	-
0.018	13%	0.02	30	0.01	60	0.005	120
0.052	26%	0.02	15	0.01	30	0.005	60

25 mmol/l of formic acid is added. The cathode is oxidized for 2 hr at 8 V vs. Ag/AgCl and the surface area is 100 cm²

Table I shows the current efficiencies when the initial selenium concentration is 2 ppm. The electrode that is electro-oxidized for 2 hr under 8 V vs. Ag/AgCl is used. The current efficiency is under 20 % when the current density is 0.167 mA/cm², but it increases more than 40 % when the current density is 0.0333mA/cm². However, the remaining selenium concentration is 1 ppm or larger, in these cases.

From the above-mentioned tendencies, it is effective to decrease the current density for increasing the current efficiency. However, the electrolysis time becomes longer with the current becoming small, so it is also effective to increase the electrode surface area to decrease the current density. Selenium concentration decreases with the progress of electrolysis, so it is also effective to decrease the current with the progress of electrolysis.

Table II shows the current efficiency when the initial selenium concentration is 2 ppm. The electrode, whose surface area is 100 cm², is used. This electrode is electro-oxidized for 2 hr at 8.0 V vs. Ag/AgCl. The electrolysis current is changed once or twice during the electrolysis. When the remaining selenium concentration is larger than 0.1 ppm, the current efficiency is larger than 30 %, but the current efficiency is 20-30 % when the remaining selenium concentration is smaller than 0.1 ppm.

4. Conclusion

Selenate ion is reduced by the electrolysis on the titanium oxide cathode, which is made by the electro-oxidation of the titanium metal plate, and selenium is removed from the model wastewater as amorphous selenium. The current efficiency more than 80-90 %, can be got when the initial selenium concentration is 50 ppm. The maximum current efficiency decreases with the initial selenium concentration becoming small, but the more than 20 % of current efficiency can be got when the initial selenium concentration is 2 ppm and the final selenium concentration is less than 0.1 ppm.

The titanium oxide electrode, which is made by the electro-oxidation of titanium metal plate, is shown to be suitable for the selenate ion removal.

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