Redox Reaction of Anions on Smectite-modified Electrode

Eriko Shimada, Koji Goto, Yasuro Ikuma and Koji Tachibana*

Department of Applied Chemistry, Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-0292, Japan

Fax:81-0462-42-8760, e-mail:shimada@chem.kanagawa-it.ac.jp

*Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162-0825, Japan

We investigated the redox reaction kinetics of anions on the smectite-modified electrodes in neutral aqueous solutions and compared it to that of cations. The cyclic voltammogram of $Fe(CN)_{6^4}/Fe(CN)_{6^3}$ measured on the modified electrode showed clearer redox waves than on a bare Pt electrode. The rate constants found for $Fe(CN)_{6^4}/Fe(CN)_{6^3}$ at the modified electrode were estimated to be 3.8×10^{-4} and 3.7×10^{-4} cm/s, respectively, being approximately ten times as large as those of Fe^{2+} and Fe^{3+} .

key words: smectite, modified electrode, redox reaction of anions, intercalation

1.INTRODUCTION

Smectite is a clay that can be intercalated with cations. These clays are used as catalysts based on their properties, therefore, there has been much research on the intercalation of cations into the clays^{1),2),3),4)}. While some studies are reported for the electrochemical behavior of cations at clay-modified electrodes, few studies concern anions. The driving force of the intercalation for smectite is considered to be the electrostatic attraction between the cationic guests and anionic hosts of the smectite's aluminosilicate layers. On smectite-modified electrodes, anions must freely migrate while the cations are attracted and caught by the negatively charged smectite layers. Using metal electrodes in neutral aqueous solutions, the electrochemical behavior of anions is sometimes masked by the specific adsorption of anions on the electrodes. Smectite-modified electrodes may enable the redox reactions of anions to be clearly observed without being disturbed by the specific adsorption of anions.

We investigated the electrode reaction kinetics of anions on smectite-modified electrodes in neutral aqueous solutions and compared them with the cation results. Using cyclic voltammetry, the kinetic parameters of $Fe(CN)_6^4/Fe(CN)_6^3$ as an anion-redox pair were estimated. Fe^{2+}/Fe^{3+} was used as a cation-redox pair for comparison. The objective of the present work is to determine the kinetic parameters of the anion-redox reactions at the smectitemodified electrode, the diffusion coefficient of the reactant (D) and the rate constant of the electrode reaction (k), and to verify that such an electrode is sensitive for anion-redox reactions in neutral solution.

2.EXPERIMENTAL

2.1 Smectite-modified electrode

The smectite used in this work was hydrothermally synthesized saponite (Smecton-SA', Kunimine Industries Co., Ltd.), with the following chemical composition [$(Si_{7.20} Al_{0.80})$ (Mg5.97Al_0.03) O₂₀ (OH)₄]^{0.77} (Na0.49 Mg0.14)^{+0.77}.

The colloidal smectite dispersion liquid was prepared from the supernatant of 300 ml of deionized water containing 10.0g of smectite powder after centrifugation. The electrode was made of Pt foil covered with an insulator resin on one side. A smectite-modified electrode was made by casting a drop of the colloidal smectite dispersion onto a Pt electrode (6.0mm diameter) and then drying for 1 day to form the film. A very thin smectite film was required in order to homogeneously supply the reactant ions from the solution for the electrode reaction.



cathodic

Fig. 1 Cyclic voltammograms of $Fe(CN)_{6}^{4/3}$ system on Pt electrodes. Scan rate: 0.05 V/s (a), 0.10 V/s (b), 0.20V/s (c), 0.5V/s (d).



Fig. 2 Cyclic voltammograms of $Fe(CN)e^{4/3}$ system on the smectite-modified electrodes. Scan rate: 0.05 V/s (a), 0.10 V/s (b), 0.20V/s (c), 0.5V/s (d).

2.2 Cyclic voltammetry

Reagent grade chemicals and deionized water were used for the electrochemical measurements.

The aqueous solutions containing 0.1 mol/dm³ Na₂SO₄ as the supporting electrolyte and test ions were degassed with nitrogen. The solution of test anions contained 0.01 mol/dm³ K₄Fe(CN)₆ and 0.01 mol/dm³ K₃Fe(CN)₆. The solution of test cations contained 0.001mol/dm³ FeCl₃ and 0.001mol/dm³ FeCl₂. The test cation solution was diluted and showed a similar current sensitivity as the test anion solution because the cations redox waves were too high at 0.01mol/dm³. The concentrated cations in the clay film due to the selective cation intercalation may react and show a higher current than the anions at the same test ions solution concentration.

The cyclic voltammetry was carried out at room temperature using a Pt wire counter electrode and a Ag/AgCl saturated KCl reference electrode saturated with KCl at scan rates between 0.05 and 0.5V/s.

3.RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms measured for $Fe(CN)6^{4}/Fe(CN)6^{3}$ at the bare Pt electrode. In the voltammograms, the $Fe(CN)6^{4}$ / $Fe(CN)6^{3}$ redox waves were not clearly observed. This was considered to be caused by the specific adsorption of anions ($SO4^{2}$, $Fe(CN)6^{3}$ and $Fe(CN)6^{4}$) onto the surface of the Pt electrode in a neutral dilute solution. The redox waves Fe^{2+}/Fe^{3+} at the modified electrode were irreversible and clearer than at the Pt electrode.

The cyclic voltammograms for $Fe(CN)_{6}^{4}$ / $Fe(CN)_{6}^{3}$ at the smectite-modified electrode exhibit distinct redox waves as shown in Fig. 2.



Fig. 3 Plots of i_p versus $v^{1/2}$ of the Fe(CN) $e^{4/3}$ system. The anodic reaction (\bigcirc): $i_{pa} = 3.26x$ $10^{.4}x v^{1/2}$, the cathodic reaction (\bigcirc): $i_{pc} = 3.59 \times 10^{.4} x v^{1/2}$.



Fig. 4 Plots of log i_p versus $E_p \cdot E_{1/2}$ of the $Fe(CN)_6^{4/3}$ system. The anodic reaction (\bigcirc): log $i_{pa} = 1.30x \ 10x \ (E_{pa} \cdot E_{1/2}) \cdot 4.63$, the cathodic reaction (\bigcirc): log $i_{pc} = 1.39x \ 10x \ (E_{pc} \cdot E_{1/2}) \cdot 4.64$.

As the scan rate (v) increased, the peak current (i_p) increased with a small shift in the peak potential (E_p) apart from the formal potential $(E_{1/2})$. Both the anodic and cathodic peak currents were proportional to $v^{1/2}$ (Fig.3), showing a diffusion controlled shape. The electrode reactions were then analyzed by using the following equations (at $25^{\circ}C)^{5}$),

 $i_{p} = 299(\alpha n_{a})^{1/2} AD^{1/2} Cv^{1/2}$ (1) $i_{p} = 0.227 \times 10^{3} n FACk \exp[\alpha n_{a} F/RT(E_{p}-E_{1/2})]$ (2)

where A is the electrode surface area, C is the concentration of the reactant in bulk, α is the transfer coefficient, n_a is the number of electrons for the rate-determining step, n is the total number of electrons for the reaction, F is Faraday's constant, R is the gas constant and T is the temperature. The other characters are as already described.

The slopes and intercepts of the plots of i_p vs. $v^{1/2}$ and log i_p vs. E_p - $E_{1/2}$ for the anodic wave by oxidation of $Fe(CN)_6^{4}$ were not significantly different from those for the cathodic wave by reduction of $Fe(CN)_6^{3}$ (Figs. 3 and 4). In the same manner, the plots for the Fe^{2+}/Fe^{3+} couple were obtained as shown in Figs. 5 and 6. The



Fig. 5 Plots of i_p versus $v^{1/2}$ of the Fe^{2+/3+} system. The anodic reaction (\bigcirc): $i_{pa} = 6.71 \times 10^{-5} \times v^{1/2}$, the cathodic reaction (\bigcirc).



Fig. 6 Plots of log i_p versus $E_p \cdot E_{1/2}$ of the Fe^{2+/3+} system. The anodic reaction (\bullet) : log $i_{pa} = 2.50x \ 10x \ (E_p \cdot E_{1/2}) \cdot 6.81$, the cathodic reaction (\bigcirc).

Table I. Kinetic parameters for redox reactions of anions (Fe(CN) $_{6^4}$, Fe(CN) $_{6^3}$) and cations (Fe³⁺, Fe²⁺) at the smectite-modified electrode.

	D /cm²s·1	αna	k /cms ^{.1}
Fe(CN)64.	1.93x10 ⁻⁷	0.77	3.8x10 ^{.4}
Fe(CN)6 ^{3.}	$2.19 x 10^{.7}$	0.82	3.7x10 ⁻⁴
Fe ²⁺	4.26x10 ^{.7}	1.48	2.5×10^{-5}
Fe ³⁺	3.72x10 ^{.7}	1.77	9.7x10 ⁻⁶

estimated kinetic parameters for the anions and cations are summarized in Table I.

At the modified electrodes, k values for anions were about ten times as large as those for the cations. The typical values⁶⁾ of D and k, which have been determined using a bare Pt electrode in acid solution, for $Fe(CN)_{6^4}/Fe(CN)_{6^3}$. are on the same order as those for Fe²⁺/Fe³⁺ $(D:3.8 \sim 7.6 \times 10^{-6} \text{ cm}^2/\text{s}, k: 3.3 \sim 5.2 \times 10^{-2} \text{ cm/s})$. In our results, while the D values for the anions were not significantly different from those for the cations, the k values were different from each other as already mentioned. It is considered that the negatively charged clay layers attracted the cations so that the cation redox reactions were much slower than the anion ones.

4.CONCLUSIONS

The redox reaction kinetics of electrode reactions of the $Fe(CN)_6^4/Fe(CN)_6^3$ anions at the smectite-modified electrode in neutral solutions were investigated by cyclic voltammetry. The redox waves of $Fe(CN)_6^4/Fe(CN)_6^3$ cleraly appeared on the modified electrode, which were not observed on the Pt electrode. It was verified that the smectite-modified electrode was sensitive to anion-redox reactions.

Using the smectite-modified electrode, the rate constant of the electrode reactions of $Fe(CN)e^{4-1}$ Fe(CN)e³⁻ were estimated to be 3.8 x 10^{-4} and 3.7 x 10^{-4} cm/s, respectively, which were ten times larger than those of Fe^{2+1}/Fe^{3+1} .

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