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# Electrochemical Behavior of Polyaniline-zeolite Composite Electrodes I. Redox of Copper-zeolites

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## Abstract

A composite electrode has been prepared by press of a mixture of zeolite and Teflonized acetylene black on platinum net and modified with a conducting polymer, polyaniline by means of electrochemical polymerization. The electrodes have been investigated for electrochemical reactions of cupric ion as a function of type of zeolite Y or A, method of ion-exchange, and solution acidity. Oxidation potential of the trapped ion at zeolite shifted considerably in the anodic direction and the shift was interpreted as the cluster size of zero valent copper ( $\text{Cu}^0$ ) resulted in an energy shift of its redox reactions. Thus copper ion participating the redox reactions should exist within the pore sites of zeolite. The electrochemical response depended strongly on solution acidity. Polyaniline interfered for copper ion to concentrate in zeolite. The mechanisms of copper ion exchange and the polyaniline modification effect were discussed on the basis of acid-base property of these substances.

## Introduction

The growing volume of publications concerning with the electrochemistry of zeolite-modified electrodes has been issued<sup>1)</sup> from the interests in chemical affinity like ionic exchange and acid-base properties and micro-selectivities like molecular sieve effect and ion selectivity. The high potentiality of zeolite for electrochemical applications, however, is limited by its insulating property and difficulty to fix it on suitable substrates. Those limitations may be related to the poor reproducibility of reactivity and weak durability of electrodes.

One important advantage in the present study is to realize a modification of zeolite with conducting polymer, polyaniline, according to electrochemical techniques. Another importance exists in stabilization of the electrochemical response and improvement of the durability of the composite electrodes by use of such conductive and stable binder as

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Teflonized acetylene black (TAB).

Polyaniline has been investigated physico-chemically in detail and proved the fibril morphology<sup>2)</sup> promising a molecule-sized microconductor. Therefore, the growth of the polymer at a boundary of the conductor and the insulator possibly creates a new zone of electrode processes.

In this paper the electrode processes of cupric ion will be described as probe reactions. Along this interest the other processes of iron species will be demonstrated in the succeeding paper<sup>3)</sup> for the generality of the function of the similar composite electrodes.

### Experimental

Zeolite Y was Linde Molecular Sieve SK-40 in NaY-powder form and zeolite A was also Linde Molecular Sieve 5A in CaA-powder form. Metal-ion-exchanged zeolite was prepared by stirring a suspension of 0.1 g of zeolite powder in 15 ml of a 0.1 M aqueous  $\text{Cu}(\text{NO}_3)_2$  solution for 24 h. Then the zeolite was filtrated and washed with water purified by Mili Q until filtrate became colorless. The exchanged zeolite is referred to as the "pre-exchanged zeolite" to distinguish from the other exchanged zeolite which is referred to as the "post-exchanged zeolite". This was prepared by dipping a composite electrode, which will be mentioned in the succeeding paragraph, consisted of non-exchanged zeolite and TAB into 0.1 M  $\text{Cu}(\text{NO}_3)_2$  solution for 24 h and then washed with water thoroughly.

For combination of zeolite powder with platinum screen substrate, TAB (Teflon 32%, acetylene black 64%) was used. Some properties of TAB have been described elsewhere<sup>4)</sup>. Certain amount of zeolite (40 mg) and TAB (20 mg) was mixed thoroughly in a mortar and prepared in a film form. The film was pressed on the both sides of the platinum screen (100 mesh). The composite electrode provided above is referred to as the "zeolite-TAB electrode".

Polyaniline was formed at the composite electrode by electrochemical polymerization of aniline (0.1 M) solved in 0.5 M  $\text{H}_2\text{SO}_4$ . The other conditions for polymerization were followed to those reported previously<sup>5)</sup>. The modified electrode is referred to as the "zeolite-TAB-PAN electrode".

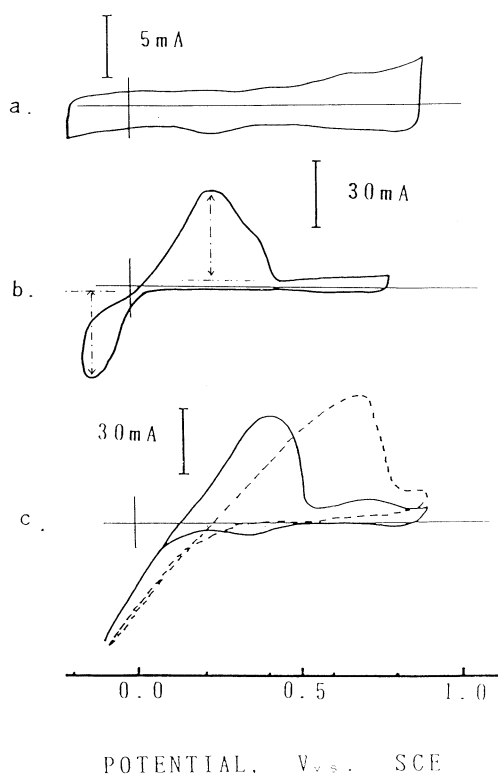
All electrochemical measurements were performed in a three compartment glass cell which contained platinum wire as a counter electrode and SCE as a reference electrode other than the test electrode in the same solution. The electrochemical equipment was a potentiogalvanostat HA-303 (Hokuto Denko Ltd.) connected with a function generator HB-111

(Hokuto Denko Ltd.). Cyclic voltammetry was performed at a constant sweep rate (50 mV/s) and at room temperature (20-24°C).

## Results and Discussion

### Cyclic voltammograms at the non-modified electrodes in acid solution

Fig. 1a shows a cyclic voltammogram (CV) at the non-exchanged zeolite-Y-TAB electrode in sulfuric acid solution. The whole feature of this CV is typically capacitive. Small peaks appearing at around 0.7 V in the anodic sweep and 0.25 V in the cathodic sweep, which can be attributed to the well-known surface processes on platinum electrode, are negligible comparing to the capacitive current.



**Fig. 1** Cyclic voltammograms in 0.5 M  $\text{H}_2\text{SO}_4$  at 50 mV/s. Electrodes: a. NeY-type zeolite-TAB; b. only TAB in the solution containing 0.05 M  $\text{Cu}(\text{NO}_3)_2$ ; c.  $\text{Cu}^{2+}$  pre-exchanged zeolite-Y-TAB (—) and post-exchanged zeolite-Y-TAB (---).

In Fig. 1b, the CV at the TAB electrode which is composed of only TAB on platinum screen demonstrates the shape of the redox reactions of cupric ion contained in the solution. The potential for the redox reactions shifts further in the negative direction than those at the two electrodes mentioned above. Since the maximum values of the current are almost the same, i. e., 41 and 39 mA at oxidative and reductive cycles, respectively, the amount of participating species to the redox reaction balances very well.

On exchanging  $\text{Na}^+$  of zeolite with  $\text{Cu}^{2+}$  the large current peaks grew up on the background of the capacitive current as shown in Fig. 1c where pre- (solid line) and post- (dashed line) exchanged zeolites

were demonstrated with solid line and dashed line, respectively. Although the shapes of both CV are almost the same, the reduction current starts at more positive potential at the pre-exchanged zeolite (0.3 V) than the post-exchanged zeolite (0.2 V). Farther the top potential of the oxidation peaks shifts about 0.3 V more positive in the anodic direction at the former than the latter. The charge values of the oxidation and reduction balance each other. This situation at the zeolite-A is totally the same to the zeolite-A.

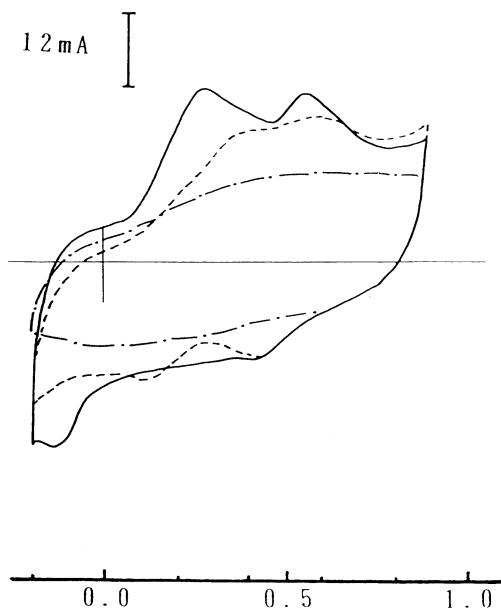
In the case of the composite electrode it is evident that cupric ion was trapped in the zeolite and the redox reaction might take place at the interfacial area between particles of zeolite and carbon contained in TAB. From the microscopic observation, carbon particles (av. 0.7  $\mu\text{m}$  diameter) are smaller in one order of magnitude than zeolite particles (Y-type zeolite : av. 7  $\mu\text{m}$  diameter). Thus the interstitial spaces of zeolite particles in the composite electrode may be closely packed with carbon particles and electrolyte solution may be supplied to the zeolite through the interstitial channels having the hydrophilic zeolite side-wall.

The values of the half wave potential of oxidation peaks of Fig. 1b and c were 0.46, 0.26, and 0.14 V for the pre- and post-exchanged zeolite and the TAB electrodes, respectively. This means that the ion trapped in zeolite is apparently more active to reduction reaction than the ion in the solution. Gion Calzaferri et al.<sup>6)</sup> have observed the same behavior on the redox of silver ion. A. Henglein<sup>7)</sup> has calculated the equilibrium potential between zero valent silver cluster and its cluster ion. According to this theory the positive shift of oxidation potential at the present system could be attributed to the greater stability of the  $\text{Cu}^0$  cluster. Thus it is suggested that the copper ion participating in the redox reactions at the composite electrode might exist at the adsorption sites of the zeolite.

**Cyclic voltammograms at the polyaniline-  
modified electrode in acid solution**

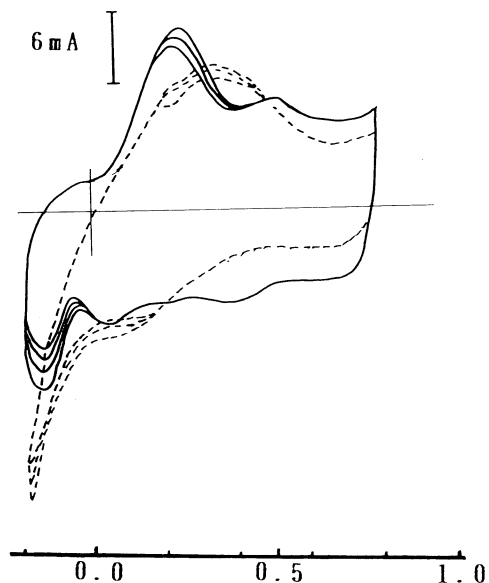
A polyaniline modification was performed at a non-exchanged zeolite-TAB electrode, providing the zeolite-TAB-PAN electrode. The CV at this electrode in sulfuric acid solution is illustrated by the dashed curve in Fig. 2. Two couples of redox peaks appear due to polyaniline redox and doping-undoping processes described as follows<sup>2)</sup>.

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POTENTIAL, V vs. SCE

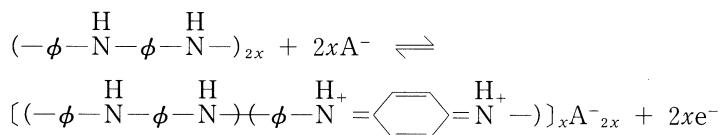
**Fig. 2** Cyclic voltammograms at  $\text{Cu}^{2+}$  post-exchanged zeolite-Y-TAB-PAN at 50 mV/s. Solution: in 0.5 M  $\text{H}_2\text{SO}_4$  (—) and 0.5 M  $\text{KNO}_3$  (---); non-exchanged zeolite-Y-TAB-PAN in 0.5 M  $\text{H}_2\text{SO}_4$  (.....).



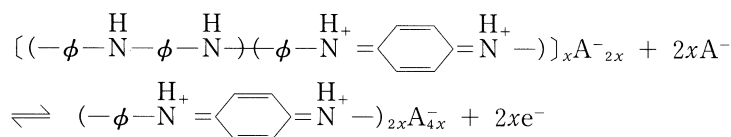
POTENTIAL, V vs. SCE

**Fig. 3** Cyclic voltammograms at  $\text{Cu}^{2+}$  post-exchanged Y-(—) and A-type (.....) zeolite modified electrodes at 50 mV/s in 0.5 M  $\text{H}_2\text{SO}_4$ .

[I].



[II].



Reaction [I] corresponds to the couple of peaks at potentials of about 0.40 and 0.13 V in the anodic and cathodic sweeps, respectively and Reaction [II] to potentials of about 0.55 and 0.40 V in the anodic and cathodic cycles, respectively.

At the post-exchanged zeolite-TAB-PAN electrode, a new couple of peaks appeared at potentials of 0.25 and -0.15 V on the anodic and cathodic CVs growing from about 0.08 V. The continuous change of those CVs was demonstrated with solid curves of Fig. 3. Comparing these CVs to those of the unmodified electrode (curves of Fig. 1), the peak positions at the post-exchanged zeolite-Y-TAB-PAN electrode are rather similar to those of the TAB electrode (Fig. 1b). Thus polyaniline may influence mainly on the affinity of the zeolite towards copper ion.

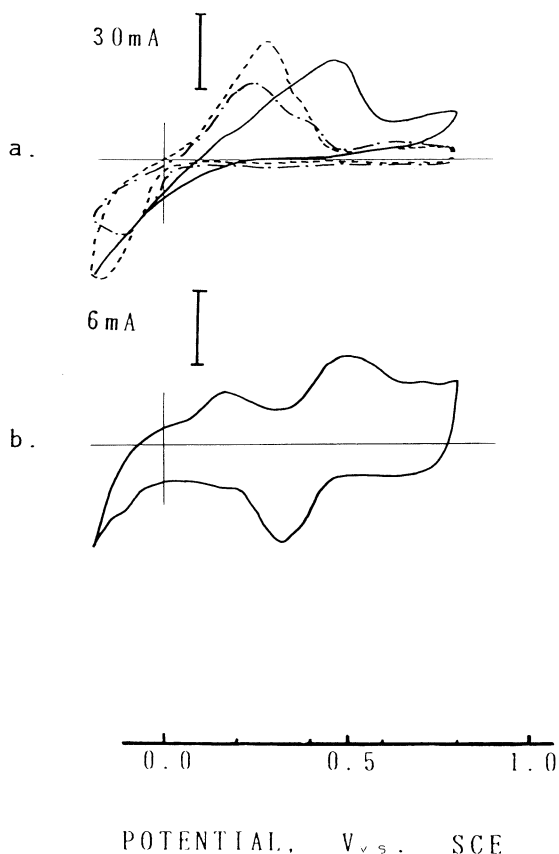
When the type of zeolite was changed to A-type (the dashed line in Fig. 3), the shape of the CV changed slightly from that of the post-exchanged zeolite-Y-TAB-PAN. In one publication<sup>9)</sup> the formation of fibers of polyaniline inside the zeolite-A-pores has been reported by use of chemical polymerization. In the present system, although polyaniline might interact with the adsorption sites of zeolite-A, the affinity still maintained in the larger level than that of the zeolite-Y possibly due to the structural difference between both zeolites.

#### **Cyclic voltammograms in neutral solution**

After the measurement in acid solution the solution was changed to the neutral one. The shape of CV changed drastically and all the current peaks disappeared at the post-exchanged zeolite-Y-TAB-PAN electrode as shown by the dashed curve with a dot of Fig. 2. In a literature<sup>2a)</sup> it has been reported that the proton doping ceases in neutral solution because polyaniline converts to an insulating polymer. On the other hand it has also known that the silver-ion-exchanged zeolite electrode combined with carbon paste behaves such a manner as peaks on CV are minimized in the range of solution pH from 5.5 to 10.2<sup>9)</sup> due to deposition of silver ion. In the present system, therefore, the disappearance of current peaks suggests two possible causes so far.: 1. disappearance of active sites on polyaniline molecular chain due to insulation and 2. decrease of cupric ion activity in the reaction zone due to deposition. The redox peaks still occur at the TAB-PAN electrode in cupric ion solution, although polyaniline redox completely disappear as shown by the dashed curve with a dot of Fig. 4a. Therefore the cause 1 can be ruled out.

In neutral solution the CV-shape at the pre-exchanged zeolite-TAB electrode (the solid curve of Fig. 4a) is essentially the same to that in an acid solution (the dashed curve of Fig.

1b). However, there appear two pairs of peaks at the post-exchanged zeolite-Y-TAB electrodes at 0.18 and 0.5 V in the anodic sweep and 0.35 and about  $-0.1$  V in the cathodic sweep as shown in Fig. 4b. But the peak current does not grow so high as those at the pre-exchanged zeolite-TAB electrodes (for example, the solid line of Fig. 4a).



**Fig. 4** Cyclic voltammograms in 0.5 M KNO<sub>3</sub> at 50 mV/s. Electrodes: a. Cu<sup>2+</sup> pre-exchanged zeolite-Y-TAB (—) in the solution without dissolved Cu<sup>2+</sup> and TAB (-----) and TAB-PAN (-·-·) in the solution containing 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub>; b. Cu<sup>2+</sup> post-exchanged zeolite-Y-TAB without Cu<sup>2+</sup> in solution.

At the TAB electrode in the neutral solution containing 0.05 M Cu(NO<sub>3</sub>)<sub>2</sub> the CV-shape is shown by the dashed line in Fig. 4a. It is the same to that in acid solution (Fig. 1c). From these results it is obvious that the activity of cupric ion in both zeolite-pores and bulk solution is not so low as all peaks disappearing and thus the cause 2 should also be canceled out.

#### The mechanisms of the ion-exchange and the modification

Thus the present study provides the first manifestation which shows the inside-polymer-zeolite by using electrochemical polymerization. In conclusion, an inductive approach leads to the following mechanisms of the ion-exchange at the present electrodes and its modification with polyaniline.

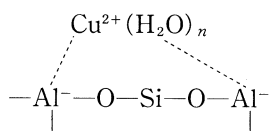
Ion exchange and acid properties of zeolite have been

ascribed to tricoordinated aluminium atoms<sup>10</sup> and silanol groups of zeolite. Hydrated cupric ion might link to the sites through ion exchange and dissociate proton under the strong influence of electrostatic field inside the zeolite cavities<sup>11</sup> as formulated by [A-1] and [A-2].

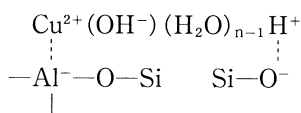


Also it is suggested that the protonated nitrogen atoms in imide radical of polyaniline molecule described in eqs. [I] and [II] can interact with the ion exchange sites of zeolite as formulated by structure [B-1]. As polyaniline hinders the ion exchange sites, the exchange capacity of the post-exchanged zeolite-TAB-PAN electrode decreases considerably as exemplified with the solid curve of Fig. 2 and the both curves of Fig. 3.

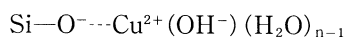
[A-1].



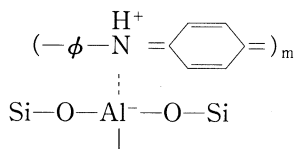
[A-2].



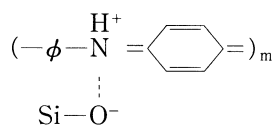
[A-3].



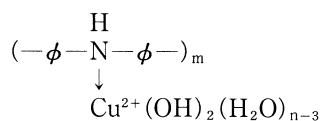
[B-1].



[B-2].



[C].



In general, silanol groups of zeolite can dissociate proton easier especially in neutral or alkaline solution and thus those might bind monohydroxy cupric ion strongly as drawn by [A-3], which might have been nominated as “deposit” owing to the anomaly low value of solubility product of  $\text{Cu}(\text{OH})_2$ . Since polyaniline has strong tendency accepting proton, the

dissociation of protons from silanol groups might be promoted at the zeolite modified with polyaniline, taking the structure [B-2].

The effect of solution neutrality, however, is completely different between the post-exchanged zeolite-Y-TAB-PAN (the dashed curve with a dot of Fig. 2) and the post-exchanged zeolite-Y-TAB (Fig. 4b) or the post-exchanged zeolite-A-TAB (the dashed curve of Fig. 5). This fact might be attributed to the surface complex formation through coordination bond between nitrogen of imide group on polyaniline and copper ion inside the zeolite cages due to the large value of stability constant of analogous complexes having N→Cu bond.

The further evidence will be provided in the next paper<sup>3)</sup> of this series.

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