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Electrocatalytic Study of Fe, Ni, Zr and Cu Complexes and Their Alumina Supported Catalysts[1]

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Abstract—The behavior of complexes of iron, nickel, zirconium and copper as an electrode in alkaline, acidic and neutral solution has been investigated primarily by cyclic voltammetry. Cyclic voltammetry is a classical measuring method in electro-analytic chemistry which is used for the study of catalysis and charge transfer. For the complexes [Fe–Cu], [Ni–Ni], [Zr–Zr] and [Cu–Cu] as well as for supported catalysts, it was possible to determine various oxidation reactions with the cyclic voltammetry method. For this method, these complexes and catalysts were coated on nickel electrodes and using cyclic voltammetry following reactions were carried out (a) oxidation of CH_3OH, (b) oxidation of NaCl and (c) oxidation of NaOH. The cyclic voltammogram presented in this work were shown to have different oxidation states and reduction states depending upon the kind of chemical reaction carried out, nature of complex utilized, the nature of support as well as how the complex is bonded to the support.

Keywords: cyclic voltammetry, complex, electrocatalytic behavior, supported catalysts and electron transfer
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INTRODUCTION

Chemical reactions in catalysis involve electron transfer. Earlier it was thought that in the catalysis the electron transfer occurred very fast and is governed by the equilibrium of the reaction, however later it was realized that this transfer process is relatively slow and it can be investigated by the cyclic voltammetry. Cyclic voltammetry is a classical measuring method in electro-analytic chemistry which can be used for the study of catalysis. Traditionally, the cyclic voltammetry determines the charge transfer between two electrodes and voltammetric experiments provide the kinetics of electron reactions involving homogeneous as well as heterogeneous transfer. The determination of reactive intermediates and kinetic analysis can reveal the nature of redox system. In view of this scientists are now using cyclic voltammetry technique in adsorption process, electro-crystallization phenomenon and charge-transfer reactions at semiconductor electrodes and that of nonmiscible electrolytes in addition to the study of homogeneous and heterogeneous reactions [1].

In [2], corrosion of metals in alcohol is reported as a good example for electrochemical reactions. In this study, the anodic oxidation of metal surfaces was determined for anodes of Cu, Zn, Fe, Ni, Al and Ti in methanol solution or their electrolytes. On the basis of the electrochemical measurements (linear sweep voltammetry, electrochemical impedance spectroscopy), spectroscopic investigations (X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and low-energy electron diffraction) and scanning electron microscopy techniques, the role of metal–alcohol intermediates in the formation of surface and soluble compounds was determined. The practical application of electrochemical etching of metals as a method of production of micro- and nanoparticles of metals and oxides is also shown.

Cyclic voltammetry method is also useful to gain information regarding the anodic properties of metals in alcoholic solutions of electrolytes. It also has noteworthy meaning in some industrial applications such as in surface treatment, obtaining metallic and composite layers or nanoparticles of metals. A large number of investigations are done [3–7] for the study of anodic properties of metals in solvents such as alcoholic solutions, although the mechanism of the reaction in these solvents is scantily predicted.

Metallophthalocyanines and other macrocyclic transition metal complexes are well known electrocatalysts for both homogeneous and heterogeneous chemical reactions. In the case of oxidations, the reaction is promoted by molecular oxygen and mediated by phthalocyanine, which interacts with the molecule to

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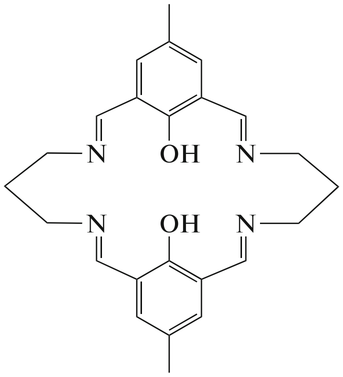


Fig. 1. Robson ligand formed by reacting two molecules of 2,6-diformyl-4-methylphenol and two molecules of 1,3-propanediamine.

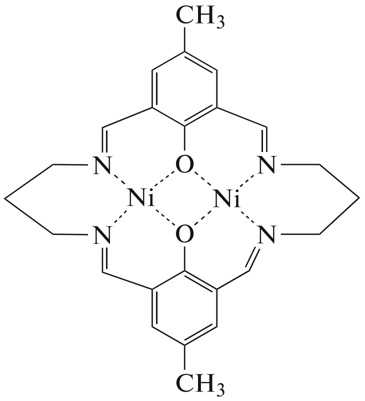


Fig. 2. [Ni–Ni] macrocomplex.

be oxidized. It is observed that if the metallophthalocyanine transition metal complex is bound to an electronic conductive surface such as an electrode, a catalytic activity for an electrochemical reaction will also be there [8].

N. Roznyatovskaya et al. [9] studied aqueous electrochemistry of binuclear copper complex with Robson-type ligand by cyclic voltammetry at highly oriented pyrolytic graphite, glassy carbon and gold electrodes.

The four electron reduction by Robson complex of oxygen has been studied and reported in the literature. The macrocyclic complexes are well known effective electro-catalysts for oxygen reduction. The complex catalysts have a configuration with a certain distance between the two metal atoms favoring interaction of oxygen with the two centers with high reactivity. The usual Robson ligand complexes (structure shown in Fig. 1) have the two metal atoms at a distance of 0.2 nm and are reported to bind to both oxygen atoms. The Ni–Ni complex (structure shown in Fig. 2) prepared is shown to have longer metal–metal distance of 0.314 nm in the adsorption layer directly at the electrode surface. The Fe–Cu complex is shown to have a metal–metal distance of around 0.4 nm [10].

Cyclic voltammetry technique is also useful in determining the heavy metals, which present in agricultural, industrial or drinking water, are a serious environmental problem. Lead is one of the most abundant heavy metals and its toxic effects cause environmental and health problems. Therefore, some of the study shown to determine the electrochemical behavior of lead(II) at poly(phenol red) modified glassy carbon electrode voltammetry technique [11].

The observations obtained from this study have shown that the oxidation and reduction states change on heterogenizing the complexes on the various supports.

COMPLEX AND CATALYST SYNTHESIS

In this study we have tested four complexes and their respective catalysts for the electro-catalytic study with cyclic voltammeter i.e. [Cu–Cu], [Zr–Zr], [Fe–Cu] and [Ni–Ni] complexes and their catalysts respectively. Complexes were prepared according to the method mentioned in Table 1.

Preparation of catalysts: The supported catalysts were prepared by the procedure discussed in our previous paper [12].

EXPERIMENTAL SETUP

All electrochemical experiments were conducted using a AUTOLAB PGSTAT 302 N, Metrohm, Netherland. It is connected to a PC running with NOVA 1.6 software. This software was used for all electrochemical data analysis. The measurements were carried out in a three electrode glass cell with separated compartments in which reference electrode used was Standard Calomel Electrode (SCE). It was connected with a cell via a Luggin capillary with saturated KCl salt bridge, and the counter electrode used was platinum foil along with the instrument. The electrolyte solutions in which electrocatalytic activity of complexes and catalysts was checked are 0.5 M NaCl, 1 M NaOH and 1 M CH_3OH + KOH solutions. Metallic nickel plate and the plate coated with different complexes and catalysts coatings were used as working electrode. Nickel electrode was cut from pure nickel (≥99.99%) sheet 0.3 mm thick. Before coating, the electrode was polished with fine emery paper. The complexes and catalysts were to be immobilized in the form of polymer film on electrode and this process was done by mixing 0.5 g of complex in 2 mL of polyvinyl alcohol (PVA) and ensures the entrapping of complex in the polymer. This paste was then applied onto the nickel electrode plate. The potential range for all experiments was maintained from –1.8 to 1.0 V, and was kept constant. Chemicals of analytical grade and triply distilled water

Table 1. Preparation steps for complex

S. no.	Complex	Step I	Step II
1	$ZrZr(OCl_2)_7$	Dialdehyde (2 g, 0.012 M) + *o*-phenylene diamine (0.65 g, 0.006 M) + zirconium oxi chloride (2.44 g, 0.012 M) all in DMF. Kept for 5 h and washed with diethyl ether. Precipitate formed and collected by filtration and dried	Precipitate from step I + *o*-phenylene diamine (0.336 g, 0.003 M) all in methanol. The precipitate obtained is the final complex
2	$NiNi \cdot H_2O$	Dialdehyde (2 g, 0.012 M) + *o*-plenylenediamine (0.65 g, 0.006 M) + nickel chloride (2.9 g, 0.012 M) all in DMF (50 mL) at 40°C. Kept for 3 h. Diethyl ether was added. Precipitate formed and collected by filtration and dried	Precipitate from step I + *o*-plenylenediamine (0.43 g, 0.004 M) in methanol (40 mL). Kept for 3 h. Diethyl ether was added. Precipitate obtained is the final complex.
3	$CuCu(CH_3COO)_2$	Dialdehyde (2 g, 0.012 M) + *o*-phenylene diamine (0.006 M, 0.65 g) + Cupric acetate (2.44 g, 0.012 M) all in DMF. Kept for 3 h and washed wth diethyl ether precipitate formed and collected by filtration and dried	Precipitate from step I + *o*-phenylene diamine (0.37 g, 0.0034 M) in methanol (40 mL). Kept for 3 h. Diethyl ether was added. Precipitate obtained is the final complex
4	$FeCu(NO_3)_3(CH_3COO)_2 \cdot H_2O$	Dialdehyde (2 g, 0.012 M) + 0.5 mL 1,3-diaminopropane (0.4 g, 0.006 M) + Ferric nitrate (2.42 g, 0.006 M), all in DMF. Kept for 5 h and washed with diethyl ether. Precipitate formed which was collected by filtration and dried. Precipitate was mixed with cupric acetate (1.5972 g, 0.008 M) in methanol. Another precipitate is formed which was washed with diethyl ether and dried	Precipitate from step I + 0.5 mL 1,3-diaminopropane (0.4 g, 0.006 M) + all in methanol. The precipitate obtained is the final complex

were used to prepare the solutions. All the experiments were carried out at room temperature (24°C).

RESULTS AND DISCUSSIONS

Cyclic voltammograms illustrate the processes of nickel surface anodic oxidation and cathodic reduction of the anodic reaction products in the solutions of 1 M NaOH, 0.5 M NaCl and 1 M CH_3OH + KOH solutions. In alkaline and neutral solutions, Ni behaves like an electropositive metal because the first anodic process is oxidation of nickel to slightly soluble hydroxide $Ni(OH)_2$ or oxide NiO as per the following reactions:

$$Ni + 2H_2O \rightarrow Ni(OH)_2 + 2H^+ + 2e, \quad (1)$$

$$Ni + 2H_2O \rightarrow NiO + 2H^+ + 2e. \quad (2)$$

Experiments Using [Ni–Ni] Complex over Nickel Electrode

Experiments in alkaline solution of 1 M NaOH. It is shown in literature that NiO and $Ni(OH)_2$ phases are formed on the Ni electrode surface in alkaline solutions [13]. The anodic and cathodic reactions are carried out at a scan rate of 10 mV/s as described in Table 2. On anodizing the passive nickel electrode in alkaline solution, two characteristic sharp peaks in anodic current appear in the voltammogram (Fig. 3). The first peak is related to the oxidation of the Ni(II) surface compounds to Ni(III) and the second one corresponding to the oxidation of ordered, compact β-$Ni(OH)_2$ phase to hydrous Ni(III) oxide (or β-NiOOH phase). This undergoes a reversible reduction and can be seen as peak A3 in Fig. 3 representing the following reaction:

$$\beta\text{-}[Ni{-}Ni](OH)_2 \leftrightarrow \beta\text{-}[Ni{-}Ni]OOH + H^+ + e. \quad (3)$$

Table 2. Anodic and cathodic reactions at various peaks for voltammogram of [Ni–Ni] complex over nickel electrode in 0.1 M NaOH solution at scan rate 10 mV/s as shown in Fig. 3 [14]

Figure 3	Cyclic voltammogram of [Ni–Ni] complex over nickel electrode in 1 M NaOH solution at scan rate 10 mV/s
A1	Oxidation peak: $Ni + 2H_2O \rightarrow Ni(OH)_2 + 2H^+ + 2e$
A2	Oxidation peak: $Ni + 2H_2O \rightarrow NiO + 2H^+ + 2e$
A3	Oxidation peak: $\beta\text{-}Ni(OH)_2 \leftrightarrow \beta\text{-}NiOOH + H^+ + e$
P	Plateau region: $Ni_3O_4 \cdot 2H_2O \quad 2NiOOH \cdot Ni(OH)_2$
A4	Oxidation peak: $Ni(OH)_2 \rightarrow NiO_2 + 2H^+ + 2e$
C1	Reduction peak: $NiO_2 + 2H^+ + 2e \rightarrow Ni(OH)_2$
C2	Reduction peak: $Ni(OH)_2 + 2H^+ + 2e \rightarrow Ni + 2H_2O$

The peak A4 represents the oxidation of Ni(II) to Ni(III) state of complex on surface electrode. In the cathodic cycle, two peaks are seen which correspond to the reduction of higher oxidation state of Ni(III) of the complex to Ni(II) of the complex. According to reference [14], the peaks beyond a potential of –1.0 V must be giving the oxidation of surface Ni(III) to Ni(IV) state of the complex. The peak which is close to 0.0 V should represent the transformation of the oxidation state 3 of nickel into dispersed phase γ-NiOOH of the complex with oxidation state between 3.5–3.7 V. Higher oxidation state of nickel is obtained when the anodic charge required for γ-NiOOH formation in the complex is divided by the amount of nickel in the surface layer. This formed γ-NiOOH phase represents a mix of NiOOH and other nickel compounds containing Ni in higher oxidation state in the complex [15]. This reference shows that the γ-NiOOH phase generally consists of 0.835 parts of NiO_2 and 0.165 parts of $Ni(OH)_2$ and the β-NiOOH phase consists of 0.75 parts of NiOOH and 0.25 parts of $Ni(OH)_2$. In alkaline medium, the formation of γ-NiOOH phase leads to the low voltage plateau (P) in the voltammetric response as shown in Fig. 3. The plateau can be depicted by the hydrous phase $Ni_3O_4 \cdot 2H_2O$ or also by $2NiOOH \cdot Ni(OH)_2$ and this phase is thermodynamically stable in our potential range of –1.8 to 1.0 V.

In the cathodic cycle, the peak C1 must correspond to the reduction of γ-phase NiOOH to Ni(III) oxidation state. Peak C2 must relate to Ni(III) to Ni(II) state reduction and peaks C3 and C4 (not shown in Fig. 3) to the reduction of β-NiOOH phase to β-$Ni(OH)_2$ phase with reversible oxidation reactions. Reduction at nickel electrode surface of NiO and $Ni(OH)_2$ to Ni is depicted by peaks C5 and C6 respectively (not shown). On comparing with the cathodic cycle, it is observed that in anodic process the main product of the reaction is O=Ni–OH phase and this is further reduced to $Ni(OH)_2$. The oxygen evolution reaction occurs on the surface of Ni electrode in alkaline medium in different ranges of potential. The mechanism of this oxygen evolution reaction in alkaline medium can be explained by the following reactions:

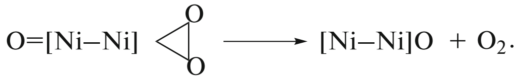
$$[Ni{-}Ni]OOH + OH^- \leftrightarrow [Ni{-}Ni]O(OH)_2 + e, \quad \text{rate determining step,} \tag{4}$$

$$[Ni{-}Ni]O(OH)_2 + 2OH^- \leftrightarrow [Ni{-}Ni]OO_2 + 2H_2O + 2e, \quad \text{rate determining step,} \tag{5}$$

$$[Ni{-}Ni]OO_2 + OH^- \rightarrow [Ni{-}Ni]OOH + O_2 + e, \quad \text{fast step,} \tag{6}$$

$$4OH^- \leftrightarrow O_2 + 2H_2O + 4e \quad \text{summary.} \tag{7}$$

According to the scheme explained, Ni(IV) peroxide in the complex acts as a direct precursor of the oxygen molecule. The main oxide taking part in the overall process and which acts as a site of reaction is hydrous Ni(III) oxide–NiOOH in the complex. For the formation of Ni(IV) peroxide from NiOOH, three electrons are transferred and hence the +6 oxidation state in $NiOO_2$ is obtained. The rate determining step of the process is step (5) which proceeds reversibly and with increasing anodic potential, the rate of step (5) increases and hence step (4) becomes the rate determining step. The nickel peroxide can decompose electrochemically reacting with OH^--group or by simple chemical decomposition step as follows [15]:



$$O{=}[Ni{-}Ni]\langle{}^{O}_{O} \longrightarrow [Ni{-}Ni]O + O_2. \tag{8}$$

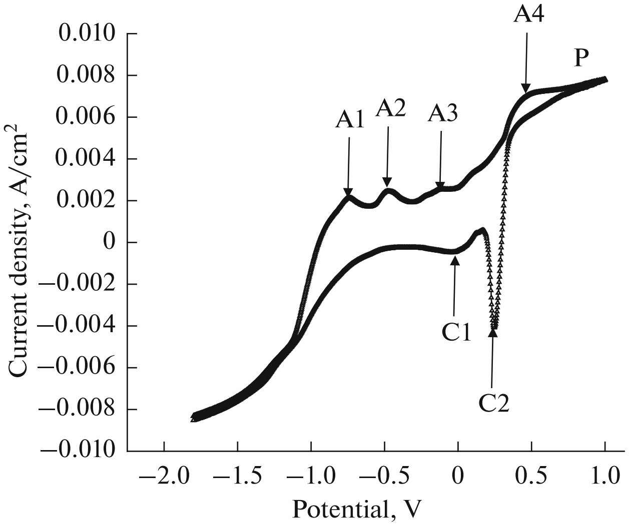


Fig. 3. Cyclic voltammogram of [Ni–Ni] complex in 1 M NaOH solution at a scan rate 10 mV/s.

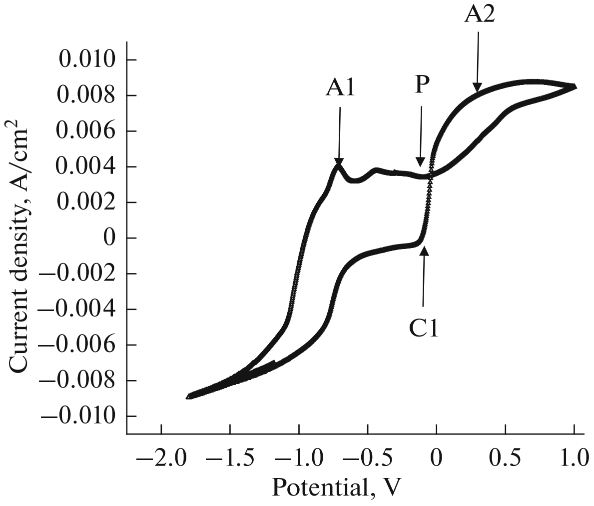


Fig. 4. Cyclic voltammogram of [Ni–Ni] complex in 0.5 M NaCl solution at a scan rate 10 mV/s.

This reaction leads to formation of $Ni_2O_3 \cdot NiO \cdot 2H_2O$ phase during the γ-NiOOH phase decomposition. The γ-NiOOH phase formed on the Ni electrode surface in alkaline solution is composed of 5 parts of NiOOH and one part of nickel peroxide. The oxidation state of Ni in this mixed phase in observed to be 3.5 which matches with the value reported in literature. Hence the experiment confirms the nickel peroxide formation on the electrode surface during the anodic process.

Experiments in neutral solution of 0.5 M NaCl. Figure 4 depicts the cyclic voltammogram in neutral medium of 0.5 M NaCl and the anodic and cathodic reactions are described in Table 3 [14]. The graph shows two oxidation peaks A1 and A2. A1 must represent the oxidation of Ni(II) to Ni(III) state (as shown in step 9) which is thermodynamically unstable. This hence reduces back to NiO_2 and is seen at the cathodic peak C1. Also a major part of the NiO in neutral media is expected to be oxidized to NiO_2 (as shown in step (10) and depicted in the graph as peak A2) and the composition of the surface layer is same as expressed by Borkowska [2] in literature. The anodic process must involve the transfer of two electrons related to the transformation of the {[Ni–Ni]$(OH)_2$ layer to anhydrous {[Ni–Ni]O_2 according to the following reaction:

$$[\text{Ni–Ni}](\text{OH})_2 \rightarrow [\text{Ni–Ni}]\text{O}_2 + 2\text{H}^+ + 2\text{e}. \quad (9)$$

In the anodic process, at the first peak, dissolution of nickel phase occurs and hydrated Ni_2^+ ions in the complex are formed. In the second anodic peak, passivation of nickel begins which is depicted by a minor cathodic current wave confirming reduction of the passivating layer. The nickel electrode is oxidized and at this potential, restructuring and dehydration of the passivating layer occurs. Hence the reduction becomes difficult and is suggested by decrease in cathodic current wave. In the cathodic process a reduction step is seen at a shift towards negative potential and it should represent the reduction of Ni_2^+ ions in the complex to Ni with intermediate reversible oxidation. In neutral medium, anhydrous NiO_2 is stable and passivation of nickel electrode surface occurs and [Ni–Ni]O_2 acts as a site for oxygen evolution reaction. At high potential values, oxidation of NiO_2 to highly unstable [Ni–Ni]O_3 (Ni(VI) oxide) occurs and it

Table 3. Anodic and cathodic reactions at various peaks for voltammogram of [Ni–Ni] complex over nickel electrode in 0.5 M NaCl solution at scan rate 10 mV/s as shown in Fig. 4 [13]

Figure 4	Cyclic voltammogram of [Ni–Ni] complex over nickel electrode in 0.5 M NaCl solution at scan rate 10 mV/s
A1	Oxidation peak: $NiO_2 + H_2O \rightarrow NiO_3 + 2H^+ + 2e$ (highly unstable)
P	Plateau region: $NiO_3 \rightarrow NiO_2$
A2	Oxidation state: $NiO + H_2O \rightarrow NiO_2 + 2H^+ + 2e$
C1	Reduction peak: $NiO_3 + 2H^+ + 2e \rightarrow NiO_2 + H_2O$

Table 4. Anodic and cathodic reactions at various peaks for voltammogram of [Ni–Ni] complex over nickel electrode in 1 M CH_3OH + KOH solution at scan rate 10 mV/s as shown in Fig. 5 [2]

Figure 5	Cyclic voltammogram of [Ni–Ni] complex over nickel electrode in 1 M CH_3OH + KOH solution at scan rate 10 mV/s
A1	Oxidation peak: $Ni + CH_3OH \rightarrow \{NiOCH_3\}_s + e + H^+$
A2	Oxidation peak: $\{NiOCH_3\}_s + CH_3OH \rightarrow \{Ni(OCH_3)_2\}_s + H^+ + e$
P1	Plateau region: $\{Ni(OCH_3)_2\}_s$
A3	Oxidation peak: $Ni + 2H_2O \rightarrow NiO + 2H^+ + 2e$
P2	Plateau region: $\{NiOCH_3\}_s$
C1	Reduction peak: $\left\{Ni\,(OCH_3)_2\right\}_s + H^+ \rightarrow NiOCH_3^+ + CH_3OH$
C2	Reduction peak: $NiOCH_3^+ + H^+ \rightarrow Ni^{2+} + CH_3OH$

immediately transforms to NiO_2. Thus, the oxidation of water molecules, OH^- ions, or more precisely O_2^- ions to molecular oxygen on the surface of nickel oxide electrodes is an electrocatalytic process carried out by nickel surface oxygen compounds.

Experiments in alkaline Methanol solution. The reversible reduction reactions taken place when our [Ni–Ni] complex coated over nickel electrode is used can be seen in Table 4 and Fig. 5. Activation of nickel surface in anhydrous CH_3OH–KOH takes place at potential higher than 0.2 V and is accompanied by etching of the layer. The passive layer is stabilized by the increase in methoxy group's concentration. Active-passive transition is controlled by surface one-electron charge transfer reaction, which can be concluded from the linear relationship of anodic peak current density to potential scan rate. Passivation of nickel in anhydrous methanol–KOH solutions has been shown in Fig. 5 can be described with the following reactions:

$$[Ni{-}Ni] + CH_3OH \rightarrow \{NiOCH_3\}_s + e + H^+, \tag{10}$$

$$\{[Ni{-}Ni]OCH_3\}_s \rightarrow [Ni{-}Ni]OCH_3^+ + e \ \text{(dissolution anodic peak)}, \tag{11}$$

$$\{[Ni{-}Ni]OCH_3\}_s + CH_3OH \rightarrow \{[Ni{-}Ni]\,(OCH_3)_2\}_s + H^+ + e \ \text{(passivation)}. \tag{12}$$

These three oxidation reactions are depicted by peaks A1, A2 and A3 in Fig. 5 and the $\{[Ni{-}Ni](OCH_3)_2\}_s$ remains stable and forms a plateau region P1 before the electrode surface undergoes oxidation to Ni(II) state. The surface nickel also undergoes oxidation with methanol to give the stable group $\{[Ni{-}Ni]OCH_3\}_s$ which is seen at plateau region P2 before undergoing further oxidation to final stable state of $\{[Ni{-}Ni](OCH_3)_2\}_s$. In Fig. 5, the reduction peaks shift towards positive potential values. This reduction in charges implies that the peaks appear not only because of the reduction of Ni(II) to Ni(III) but also due to the reduction of nickel species in hydrous oxide form formed at first peak. The positive shift suggests that the reduction of nickel species is not affected. The presence of hydrogen ions stimulates the activation of nickel surface trough removing methoxy groups:

$$\begin{gathered}\left\{[Ni{-}Ni](OCH_3)_2\right\}_s + H^+ \\ \rightarrow [Ni{-}Ni]OCH_3^+ + CH_3OH,\end{gathered} \tag{13}$$

$$[Ni{-}Ni]OCH_3^+ + H^+ \rightarrow Ni^{2+} + CH_3OH. \tag{14}$$

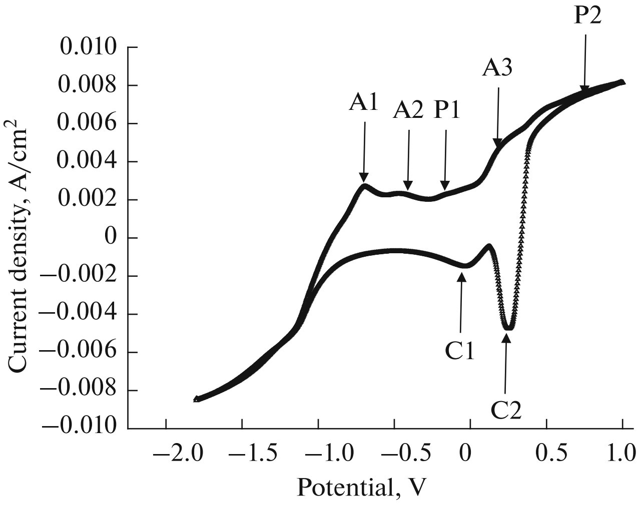


Fig. 5. Cyclic voltammogram of [Ni–Ni] complex in 1 M CH_3OH + KOH solution at a scan rate 10 mV/s.

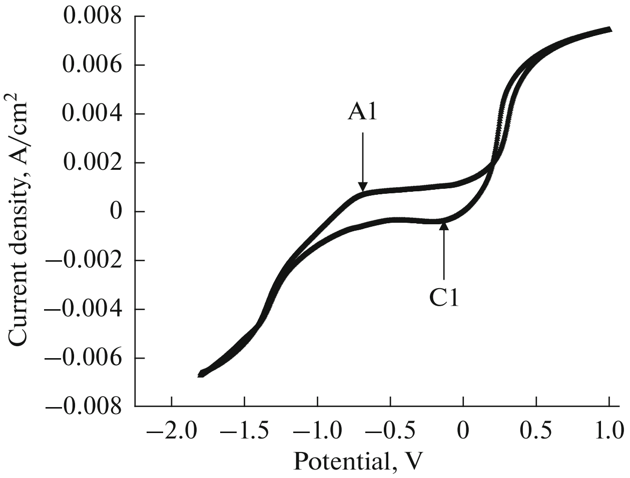


Fig. 6. Cyclic voltammogram of [Ni–Ni]/Al_2O_3 complex catalyst in 1 M CH_3OH + KOH solution at a scan rate 10 mV/s.

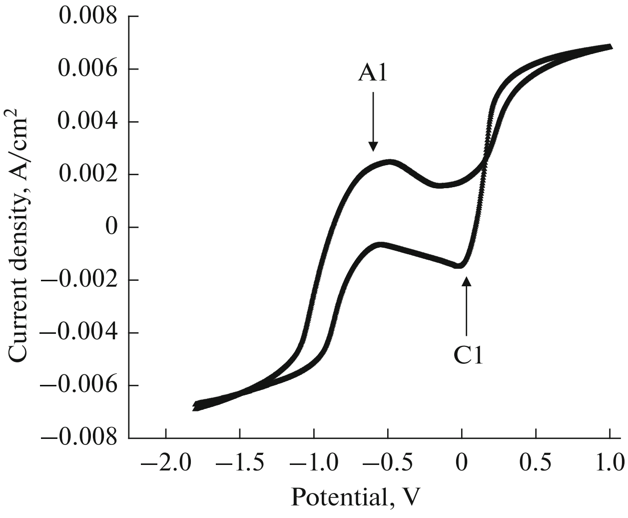


Fig. 7. Cyclic voltammogram of [Ni–Ni]/Al_2O_3 complex catalyst in 0.5 M NaCl solution at a scan rate 10 mV/s.

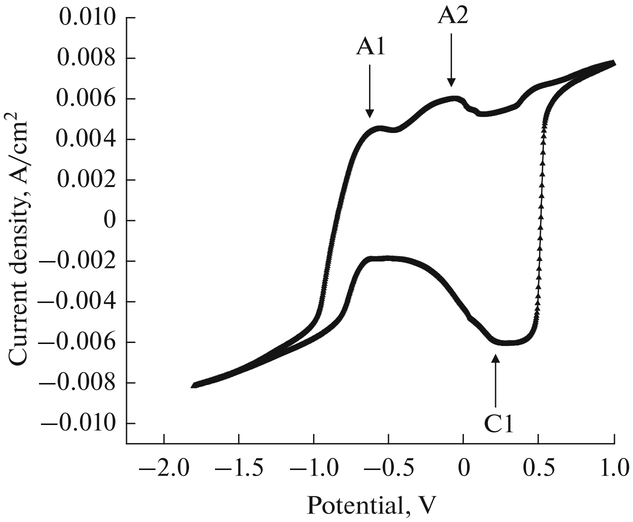


Fig. 8. Cyclic voltammogram of [Ni–Ni]/Al_2O_3 complex catalyst in 1 M NaOH solution at a scan rate 10 mV/s.

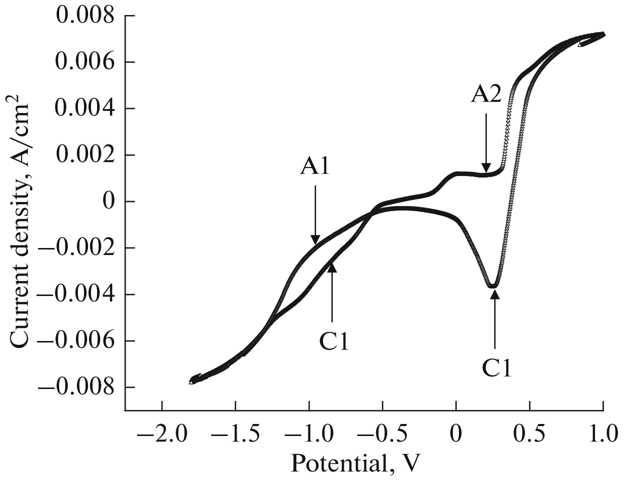


Fig. 9. Cyclic voltammogram of [Fe–Cu] complex in 1 M NaOH solution at a scan rate 10 mV/s.

These two steps show the cathodic peaks at C1 and C2 respectively formed in the reduction reaction. The cathodic process shows the reduction of Ni^{2+} to Ni and oxidizing the methanol ions.

Similarly, electrocatalytic experiments were done with the catalysts [Ni–Ni]/Al_2O_3 by using 1 M CH_3OH + KOH, 0.5 M NaCl and 1 M NaOH solutions as electrolyte. Oxidation peaks and reduction peaks are shown in Figs. 6–8.

Experiments Using [Fe–Cu] Complex over Nickel Electrode

Experiments in alkaline solution of 1 M NaOH. The [Fe–Cu] complex was coated on Nickel plate, the oxidation reduction process observed in 1 M NaOH solution at a scan rate of 10 mV/s is given in Fig. 9 and the anodic and cathodic reactions are given for this process in Table 5. Figure 9 shows the oxidation states of Fe and Cu in the complex at the electrode surface and it is identical to the oxidation-reduction of Fe plate at anode [16]. This reference also gives the oxidation-reduction of Cu plate at the anode and the peaks A2 and C2 observed in our results as shown in Fig. 6, are also identical to those for copper plate as anode. This also suggests that in the oxidation reduction process for our complex, when Fe is in the oxidation state, the Cu in it is in the reduction state. The anodic and cathodic reactions are described in Table 5 which means that A1 corresponds to oxidation of Fe, C1 to

Table 5. Anodic and cathodic reactions at various peaks for voltammogram of [Fe–Cu] complex over nickel electrode in 0.1 M NaOH solution at scan rate 10 mV/s as shown in Fig. 9 [16]

Figure 9	Cyclic Voltammogram of [Fe–Cu] complex over nickel electrode in 1 M NaOH solution at scan rate 10 mV/s
A1	Oxidation peak: $Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e$
C1	Reduction peak: $Fe(OH)_2 + 2e \rightarrow Fe + 2OH$
A2	Oxidation peak: $2Cu + 2OH^- \rightarrow Cu_2O + H_2O + 2e$
C2	Reduction peak: $Cu_2O + H_2O + 2e \rightarrow 2Cu + 2OH$

the reduction of $Fe(OH)_2$. A2 is the oxidation of Cu and C2 is the reduction of $Cu(OH)_2$.

Experiments in Neutral 0.5 M NaCl Solution

The cyclic voltammogram of [Fe–Cu] complex deposited on Nickel plate is also carried out in presence of 0.5 M NaCl solution at a scan rate of 10 mV/s and is given in Fig. 10. This figure gives the oxidation states of Fe and Cu in the complex at the electrode surface. The oxidation states of Fe electrode for this solution show the presence of three anodic peaks and two cathodic peak [17] and all these peaks can be observed in Fig. 7. Therefore for our complex, the first anodic peak the oxidation of Fe occurs; at the second peak oxidation of Cu occurs and at the third oxidation peak oxidation of $Fe(OH)_2$ and $Cu(OH)_2$ occur. Similarly for the Cu electrode, literature suggests two oxidation states which seem to imply there is an overlap for our complex at A3 of Fig. 7 and both Fe and Cu are getting oxidized. During the cathodic cycle, the reduction of Fe and Cu occurs to give oxidation state of +2 at peak C1. The anodic and cathodic reactions are described in Table 6.

Experiments in alkaline methanol solution. The cyclic voltammogram of [Fe–Cu] complex over nickel electrode in 1 M ofmethanol + KOH is shown in Fig. 11 and the anodic and cathodic reactions are tabulated in Table 7. The literature for Fe electrode gives same peaks as observed by us in Fig. 8. In view of this, peak A1 in the figure shows that the Fe is oxidized to Fe(II) and methanol is oxidized leading to hydrogen evolution, as explained in [2]. Similarly in our case, at peaks A2 and A3, the passivation of methoxide layer is observed and at the peak C1, methoxide film is removed giving FeO. Literature reports no reaction of Cu electrodes with methanol, which means that in our complex the Cu is not playing any role in the reaction. The passivation reaction of Fe in anhydrous methanol–KOH solution can be described with following reactions:

Hydrogen evolution and formation of methoxy group:

$$Fe \rightarrow Fe^{2+} + 2e, \quad (15)$$

$$CH_3OH \rightarrow CH_3O^- + 1/2\,H_2. \quad (16)$$

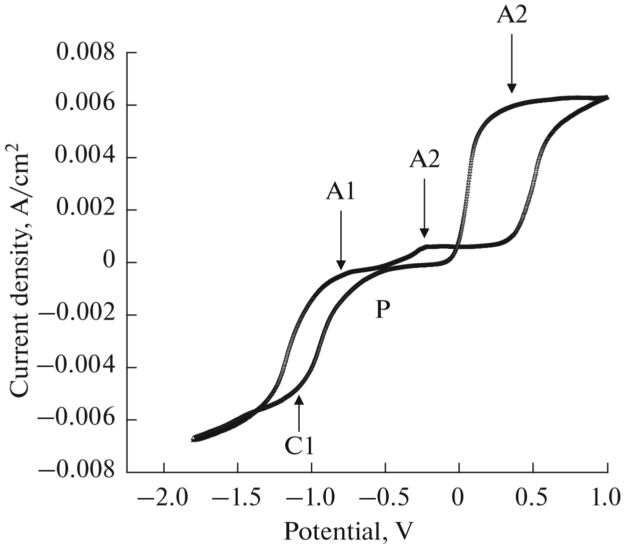


Fig. 10. Cyclic voltammogram of [Fe–Cu] complex in 0.5 M NaCl solution at a scan rate 10 mV/s.

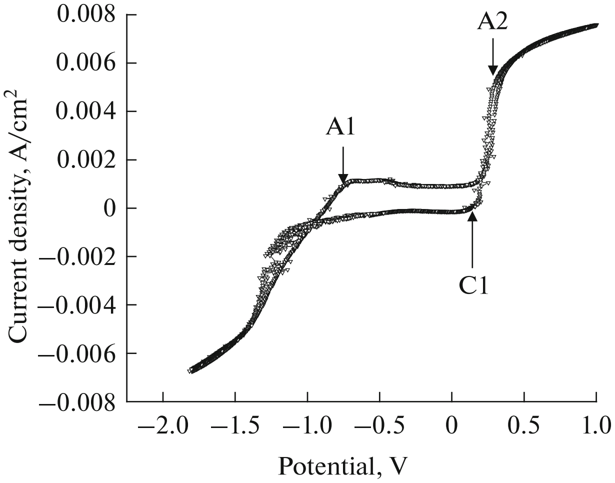


Fig. 11. Cyclic voltammogram of [Fe–Cu] complex in 1 M CH_3OH + KOH solution at a scan rate 10 mV/s.

Table 6. Anodic and cathodic reactions at various peaks for voltammogram of [Fe–Cu] complex over nickel electrode in 0.5 M NaCl solution at scan rate 10 mV/s as shown in Fig. 10 [16, 17]

Figure 10	Cyclic voltammogram of [Fe–Cu] complex over nickel electrode in 0.5 M NaCl solution at scan rate 10 mV/s
A1	Oxidation peak: $Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e$ $Fe(OH)_2 + OH^- \rightarrow FeOOH + e$
A2	Oxidation peak: $2Cu + 2OH^- \rightarrow Cu_2O + H_2O + 2e$ $Cu_2O + 2OH^- \rightarrow 2CuO + H_2O + 2e$
A3	Oxidation peak: $3Fe(OH)_2 \leftrightarrow Fe_3O_4 + 2H_2O + 2H^+ + 2e$ $2Cu(OH)_2 \leftrightarrow Cu_2O_3 + H_2O + 2H^+ + 2e$
C1	Reduction peak: $Fe_3O_4 + 2H_2O + 2H^+ + 2e \leftrightarrow 3Fe(OH)_2$ $Cu_2O_3 + H_2O + 2H^+ + 2e \leftrightarrow 2Cu(OH)_2$
C2	Reduction peak: $Fe(OH)_2 + 2e \leftrightarrow Fe + 2OH^-$ $2Cu(OH)_2 + 2e \leftrightarrow Cu + 2OH^-$

Table 7. Anodic and cathodic reactions at various peaks for voltammogram of [Fe–Cu] complex over nickel electrode in 1 M CH_3OH + KOH solution at scan rate 10 mV/s as shown in Fig. 11 [2]

Figure 11	Cyclic voltammogram of [Fe–Cu] complex over nickel electrode in 1 M CH_3OH + KOH solution at scan rate 10 mV/s
A1	Hydrogen evolution and formation of methoxy group: $Fe \rightarrow Fe^{2+} + 2e$ $CH_3OH \rightarrow CH_3O^- + 1/2H_2$
A2	Passivation of methoxide layer: $Fe^{2+} + 2CH_3O^- \rightarrow Fe(OCH_3)_2$
C1	Removal of methoxide film: $Fe(OCH_3)_2 \rightarrow FeO + CH_3OCH_3$

Passivation of methoxide layer:

$$Fe^{2+} + 2CH_3O^- \rightarrow Fe(OCH_3)_2. \quad (17)$$

Removal of methoxide film:

$$Fe(OCH_3)_2 \rightarrow FeO + CH_3OCH_3. \quad (18)$$

Similarly, electrocatalytic experiments were done with the catalysts [Fe–Cu]/Al_2O_3 by using 1 M CH_3OH + KOH, 0.5 M NaCl and 1 M NaOH solutions as electrolyte. Oxidation peaks and reduction peaks are shown in Figs. 12–14.

Electrovoltammetric Studies of Different Macrocyclic Complexes and Supported Catalysts

In the Table 8, we have listed the results of cyclic voltammograms of the other complexes [Zr–Zr], [Cu–Cu] and their respective catalysts supported on alumina by using 1 M CH_3OH + KOH, 0.5 M NaCl and 1 M NaOH solutions as electrolyte. From the table it is clear that CH_3OH_4 oxidation in presence of KOH is occurred by [Zr–Zr] complex where there are two oxidation states A1, A2 and two reduction states C1, C2. When the reaction is changed to NaCl and number of oxidation states reduced to one and reduction states are also reduced to one. One reducing state

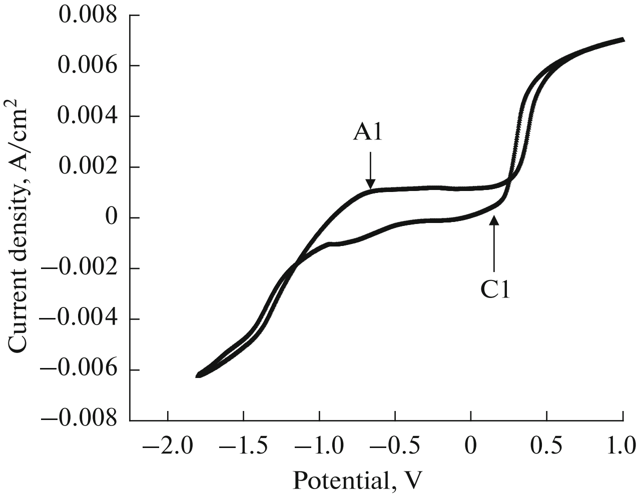


Fig. 12. Cyclic voltammogram of [Fe–Cu]/Al_2O_3 complex catalyst in 1 M CH_3OH + KOH solution at a scan rate 10 mV/s.

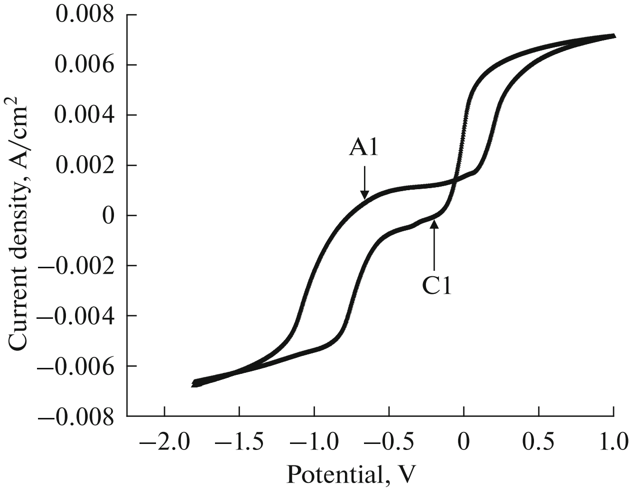


Fig. 13. Cyclic voltammogram of [Fe–Cu]/Al_2O_3 complex catalyst in 0.5 M NaCl solution at a scan rate 10 mV/s.

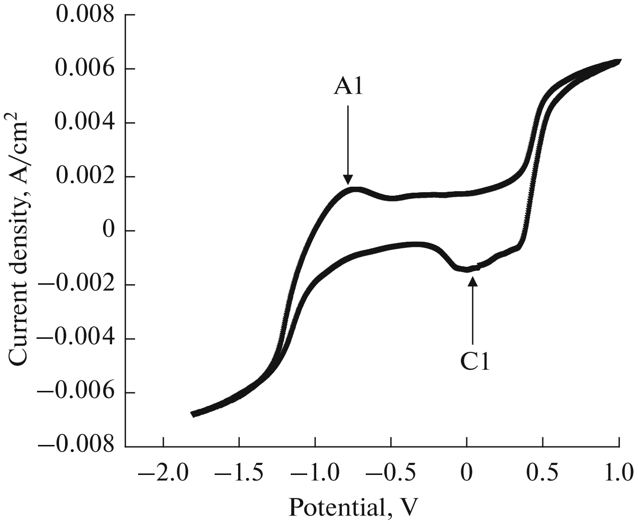


Fig. 14. Cyclic voltammogram of [Fe–Cu]/Al_2O_3 complex catalyst in 1 M NaOH solution at a scan rate 10 mV/s.

is there with NaOH while the oxidation states are same as in the previous case. It is also shown in table that, there is only one oxidation as well as reducing state for the complex [Cu–Cu] using different electrolytes such as CH_3OH + KOH, NaCl and NaOH.

Similarly, effect of variation of reaction with different electrolytes such as CH_3OH + KOH, NaCl and NaOH has been shown, for [Zr–Zr]/Al_2O_3 and for [Cu–Cu]/Al_2O_3 in Table 8. From the Table 8 and results from the figures clearly show that the number of oxidation states and their position depends upon chemical reaction.

CONCLUSIONS

The chemical reactions invariably occur with transfer of electrons and are similar in nature to electrochemical reactions occurring between two electrodes. The technique of cyclic voltammetry in electrochemistry can be used for the study the electrochemical properties of heterogeneous catalysts. Assuming, the metals present in the complex react similarly as metals

Table 8. Data of cyclic voltammogrammes of various complexes and their catalyst

S. no.	Complex	Oxidation peak (potential and current)	Reduction peak (potential and current)	Electrolyte
1	[Zr–Zr]	A1 = (–1.1 V, 0.002 A) A2 = (–0.4 V, 0.001 A)	C1 = (0.25 V, –0.001 A) C2 = (–0.5 V, –0.001 A)	1 M CH_3OH + KOH
2	[Zr–Zr]	A1 = (–1 V, 0.005A)	C1 = (0.4 V, 0.005 A)	0.5 M NaCl
3	[Zr–Zr]	A1 =(–0.75 V, 0.001 A) A2 = (0.4 V, 0.005 A)	C1 = (0.25 V, –0.001 A)	1 M NaOH
4	[Zr–Zr]/Al_2O_3	A1 = (–0.80 V, 0.001 A)	C1 = (0.27 V, –0.001 A)	1 M CH_3OH + KOH
5	[Zr–Zr]/Al_2O_3	A1 = (–0.6 V, 0.001 A) A2 = (0.25 V, 0.005 A)	C1 = (0.4 V, 0.004 A) C2 = (–0.6 V, –0.001 A)	0.5 M NaCl
6	[Zr–Zr]/Al_2O_3	A1 = (–0.7 V, 0.001 A)	C1 = (–0.02 V, –0.0035 A)	1 M NaOH
7	[Cu–Cu]	A1 = (-0.75 V, 0.002 A)	C1 = (0.15 V, –0.001 A)	1 M CH_3OH + KOH
8	[Cu–Cu]	A1 = (–0.6 V, 0.003 A)	C1 = (–0.3 V, –0.003 A)	0.5 NaCl
9	[Cu–Cu]	A1 = (–0.1 V, 0.002 A)	C1 = (–0.25 V, –0.002 A)	1 M NaOH
10	[Cu–Cu]/Al_2O_3	A1 = (–0.6 V, 0.001 A)	C1 = (–0.6 V, –0.003 A)	1 M CH_3OH + KOH
11	[Cu–Cu]/Al_2O_3	A1 = (–0.2 V, 0.002 A)	C1 = (–0.1 V, –0.001 A)	0.5 M NaCl
12	[Cu–Cu]/Al_2O_3	A1 = (0.1 V, 0.0004 A) A2 = (0.75 V, 0.0006 A)	C1 = (–1 V, –0.0003 A)	1 M NaOH

in electrodes. For the complexes [Fe–Cu], [Ni–Ni], [Zr–Zr] and [Cu–Cu] as well as for supported catalysts, it was possible to determine various oxidation reactions with this method. For doing this experiment, these complexes and catalysts were coated on nickel electrodes and using cyclic voltammeter following reactions were carried out (a) oxidation of CH_3OH, (b) oxidation of NaCl and (c) oxidation of NaOH. The cyclic voltammogram presented in this work were shown to have different oxidation states and reduction states depending upon the kind of chemical reaction carried out, nature of complex utilized, the nature of support as well as how the complex is bonded to the support.

REFERENCES

1. Jurgen, H., Cyclic voltammetry–electrochemical spectroscopy–new analytical methods, *Angew. Chem., Int. Ed.,* 1983, vol. 23, p. 831.
2. Banas, J., Stypula, B., Banas, K., Mrowiecka, J.S., Starowiez, M., and Borkowska, U.L., Corrosion and passivity of metals in methanol solutions of electrolytes, *J. Solid State Electrochem.,* 2009, vol. 13, p. 1669.
3. Mandal, S.K., Adhikary, B., and Nag, K., Dinuclear metal complexes. Part 4. Electrochemical studies of macrocyclic dicopper(II) complexes. Investigation of the effect of solvents, donor groups, and steric constraints on the stability of mixed-valence copper(II)–copper(I) complexes, *J. Chem. Soc., Dalton Trans.,* 1986, vol. 6, p. 1175.
4. Banas, J., The anodic behaviour of chromium steel X20Cr13 in organic solutions of sulphuric acid, *Corros. Sci.,* 1982, vol. 22, no. 11, p. 1005.
5. Banas, J., Anodic behavior of chromium in anhydrous and water-containing dimethylformamide H_2SO_4 and methanol H_2SO_4 solutions, *Electrochim. Acta,* 1982, vol. 27, no. 8, p. 1141.
6. Banas, J., The effect of water on the anodic behaviour of Fe–Mo alloys in organic solvents, *Corros. Sci.,* 1982, vol. 22, no. 11, p. 997.
7. Danilov, A.I., Molodkina, E.B., and Polukarov, Yu.M., Initial stages of copper electrocrystallization on a glassy-carbon ring–disk electrode from sulfate electrolytes of various acidity: A cyclic voltammetry study, *J. Electrochem. Soc.,* 1986, vol. 133, no. 2, p. 253.
8. Zagal, J.H., Metallophthalocyanines as catalysts in electrochemical reactions, *Coord. Chem. Rev.,* 1992, vol. 119, p. 89.
9. Roznyatovskaya, N.V., Vassiliev, S.Yu., Yusipovich, A.I., Tsirlina, G.A., and Roznyatovskii, V.V., Aqueous electrochemistry of binuclear copper complex with Robson-type ligand: Dissolved versussurface-immobilized reactant, *J. Solid State Electrochem.,* 2005, vol. 9, p. 581.
10. Roznyatovskaya, N.V., Laurinavichute, V.K., Tsirlina, G.A., and Mirsky, V.M., Electrochemistry and catalytic behavior of immobilized binuclear complexes of copper(II) and nickel(II) with Robson type ligand, *J. Sold State Electrochem.,* 2007, vol. 11, p. 981.
11. Gongjun, Y., Xilong, Qu., Ming, S., Chengyin, W., Qishu, Qu., Xiaoya, Hu., Electrochemical behavior of lead(II) at poly(phenol red) modified glassy carbon electrode, and its trace determination by differential pulse anodic stripping voltammetry, *Microchim. Acta,* 2008, vol. 160, p. 275.
12. Biswas, Sh., Biswas, P., and Kumar, A., Catalytic cracking of soybean oil with zirconium complex chemically bonded to alumina support without hydrogen, *Int. J. Chem. Sci. Appl.,* 2012, vol. 3, no. 2, p. 306.
13. Medway, S.L., Lucas, C.A., Kowal, A., Nichols, R.J., and Johnson, D., In situ studies of the oxidation of nickel electrodes in alkaline solutions, *J. Electroanal. Chem.,* 2006, vol. 587, p. 172.
14. Juodkazis, K., Juodkazyte, J., Vilkauskaite, R., and Jasulaitiene, V., Nickel surface anodic oxidation and electrocatalysis of oxygen evolution, *J. Sold State Electrochem.,* 2008, vol. 12, p. 1469.
15. Barnard, R., Randell, C.F., and Tye, F.L., Studies concerning charged nickel hydroxide electrodes I. Measurement of reversible potentials, *J. Appl. Electrochem.,* 1980, vol. 10, p. 109.
16. Jayalakshmi, M. and Balasubramanian, K., Cyclic voltammetric behaviour of copper powder immobilized on paraffin impregnated graphite electrode in dilute alikali solution, *Int. J. Electrochem. Sci.,* 2008, vol. 3, p. 1277.
17. Muralidharan, V.S. and Veerashanmughamani, M., Electrochemical behaviour of pure iron in concentrated sodium hydroxide solutions at different temperatures: A triangular potential sweep voltammetric study, *J. Appl. Electrochem.,* 1985, vol. 15, p. 675.