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Zeolite-encapsulated M(Co, Fe, Mn)(SALEN) complexes modified glassy carbon electrodes and their application in oxygen reduction

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ABSTRACT

Zeolite-encapsulated transition metal complexes of SALEN [N, N′-bis(salicylidene) ethylenediamine] have been used as catalysts of oxidation reactions of hydrocarbons with oxidants including dioxygen. But in these processes molecular oxygen as oxidant did not show good activity compared with other oxidants such as TBHP, PhIO and H_2O_2. In order to evaluate the catalytical effect of the hybrid materials on the process of activating molecular oxygen, zeolite-encapsulated M(Co, Fe, Mn)(SALEN) complexes modified glassy carbon electrodes [M(SALEN)/Y/GCEs (M = Mn, Fe, Co)] were prepared and used as electrocatalysts of oxygen reduction reaction (ORR). The electrocatalytic reduction of dioxygen, thus, was investigated by cyclic voltammetry (CV) and chronocoulometry (CC) at glassy carbon electrodes (GCEs) modified with metal (Co, Fe, Mn) complexes of SALEN encapsulated inside NaY in pH 6.90 aqueous solutions. The results have shown that the M(SALEN)/Y/GCEs (M = Mn, Fe, Co) exhibited efficient electrocatalytic activity towards dioxygen reduction with reduced overpotentials of about 505 mV, 393 mV and 397 mV for Co(SALEN)/Y, Fe(SALEN)/Y and Mn(SALEN)/Y, respectively, lower than bare GC electrode and enhanced peak currents. The electroreduction of O_2 on these modified GCEs is an irreversible and diffusion-controlled process. The transferred number of electrons and the transfer coefficient for dioxygen reduction reaction were determined by CV and CC. These results suggest that zeolite-encapsulated M(Co, Fe, Mn)-SALEN complexes can efficiently activate molecular oxygen by decreasing the overpotential and increasing current of oxygen reduction reaction. And dioxygen is reduced to form water in the process. The significance of this work lies in evaluating the catalysis of the hybrid catalysts for oxidation reaction by electrochemical techniques.

1. Introduction

Up to the present, there have been many reports on the preparation and characterization of zeolite-encapsulated, ship-in-a-bottle metal complexes of SALEN [N, N′-bis(salicylidene) ethylenediamine] [1–6]. The encapsulation of metallosalen complexes is usually carried out by the flexible ligand method, in which a flexible ligand, able to freely diffuse through the zeolite pores, complexes with a pre-exchanged metal ion. The resultant complex becomes too large and rigid to leave the cages. It is well known that cytochrome P-450, containing iron metal in the prosthetic active site, is capable of activating dioxygen, forming active species capable of oxidizing alkanes [7]. Therefore, the zeolite-encapsulated metallosalen complexes, a kind of biomimetic system, have been proposed as functional models of cytochrome P-450 [1,5,8,9]. They have been studied extensively as biomimetic catalysts for hydrocarbon hydroxylation/epoxidation and alcohol carbonylation with a variety of oxidants including hydrogen peroxide [1,3,4,10], tert-butylhydroperoxide (TBHP) [1,10–12,6], and iodosylbenzenes (PhIO) [9,10], and with less frequent use of O_2 as oxidant [2,5,8]. Molecular oxygen was proven not to be a good oxidant for oxidation reactions of organic compound compared with the other oxidants mentioned above [10,11] because of its higher chemical stability. Can or to what extent the zeolite-encapsulated metallosalen complexes activate molecular oxygen as cytochrome P-450 in biological process? How does the oxygen reduction reaction (ORR) conduct in the presence of these hybrid catalysts of zeolite-encapsulated metallosalen complexes as electrocatalysts? We would like to know if the zeolite-encapsulated metallosalen complexes modified glassy carbon electrodes are capable of promoting the oxygen reduction reaction in aqueous solution.

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On the other hand, oxygen reduction has been of great theoretical and practical importance in power sources, biological processes and chemical syntheses. In particular, the design and development of new catalysts for the multielectron reduction of dioxygen has received a great deal of attention for practical applications such as biological reactions and fuel cells [13–16]. There have been extensive investigations on electrochemical reduction of O_2 with electrocatalysts such as noble-metal materials such as Pt [17–20], Au [21], Ru [22], non-noble materials including inorganic oxide compounds [23,24], organic compounds such as anthraquinone and its derivatives [25–28], biological enzyme such as catalase [29,30], vitamin B [31,32] and riboflavin [33], and metal macrocyclic complexes of phthalocyanines [34,35] and porphyrins [13,36–40]. In addition, transition metal complexes of Schiff-base ligands, especially SALEN complexes [8,41–43] which may mimic the catalytic cycle of cytochrome P-450, have attracted much research interest with their easy preparation in experimental lab. As electrocatalysts for the ORR process, the complexes are often coated on the surface of glassy carbon electrode, forming modified electrodes by either electropolymerizing the complexes to obtain conducting polymer film [39,44,45] on the surface of glassy carbon electrodes, or immobilizing them into some polymer compounds, such as polypyrrole [27], polyacrylamide [30], Nafion [40,46,47] and polyaniline [48], followed by the absorption of these polymer compound on glassy carbon electrodes. In fact, chemically modified electrodes (CMEs) have continued to be of major concern during the last decade. And a relatively large amount of electrochemical research has been devoted to the development and application of different types of CMEs [49]. Zeolite-modified electrodes are a kind of important chemically modified electrodes in studying the redox behavior of the metal complexes encapsulated in zeolite. The electrochemical properties of the CMEs of zeolite-immobilized metallosalen complexes were much investigated in 1990s [50–52]. But there are only a few papers on ORR using zeolite-encapsulated metallosalen complexes as electrocatalysts [53].

In the present contribution, the NaY zeolite-encapsulated M(SALEN) modified electrodes, denoted as M(SALEN)/Y/GCEs (M = Mn, Fe, Co), were prepared and used as electrocatalysts for the ORR process. The electrochemical behavior and catalytic efficiency of these modified electrodes for ORR were examined by CV and CC.

2. Experimental

2.1. Reagents and chemicals

All chemicals and reagents used in present work were of analytical grade and used as received without further purification. All aqueous solutions for electrochemical experiments were prepared using doubly deionized water. The supporting electrolyte in organic system used for electrochemical experiments, tetra-*n*-butylammonium perchlorate (TBAP), was prepared according to literature procedure [54] and recrystallized three times, 0.025 mol l^{-1} phosphate buffer solution (pH 6.90) was purchased from Tianjin Guangfu Fine Chemicals Company in China. The used NaY was purchased from the China Petroleum and Chemical Corporation. Its SiO_2/Al_2O_3 ratio is 5.80.

2.2. Preparation of the M(SALEN)/Y(M = Co, Fe, Mn)

NaY zeolite was subjected to ion-exchange in water solutions (0.01 mol l^{-1}) of $Co(CH_3COO)_2$, $FeCl_3$ or $Mn(CH_3COO)_2$ at room temperature for two times. Washed with water several times and dried in the air, the NaMY(M = Co, Fe, Mn) was then obtained. The metallosalen complexes were synthesized inside the faujasite structure through reaction between the ion-exchanged zeolite Y (NaMY) and the SALEN ligand by flexible ligand method [55]. Typically, 0.5 g of the $NaCo^{II}Y$ and 1.5 g H_2SALEN were intimately mixed and placed in a crucible with cover. The crucible was then heated to 170 °C and kept for 24 h in air. The molten slurry was cooled to room temperature and extracted with methylene chloride, acetone and acetonitrile until the solvent was colorless to obtain the brown powder of $Co^{III}(SALEN)/Y$. Using the same method, $Fe^{III}(SALEN)/Y$ (brown red) and $Mn^{III}(SALEN)/Y$ (earth yellow) were obtained by replacing $NaCo^{II}Y$ with $NaFe^{III}Y$ or $NaMn^{II}Y$.

2.3. Preparation of working electrodes

Prior to modification, the GC electrode was polished to a mirror-like surface with alumina and water slurry on polishing cloth and rinsed with doubly distilled water. Then, it was cleaned ultrasonically in acetone, absolute ethanol, HNO_{3-} H_2O (1:1, v/v) solution and distilled water in the sequence, then dried in air before use.

The modified electrodes were prepared according to the literature [56]. To obtain the best voltammetric responses of M(SALEN)/Y composite film, the experimental conditions for film casting, such as the mass ratio of M(SALEN)/Y to graphite, the concentration of the suspension of M(SALEN)/Y and graphite in tetrahydrofuran (THF), the concentration of the solution of PS in THF, and the total volume of suspension of M(SALEN)/Y and graphite, were optimized. Typically, 30 mg of M(SALEN)/Y and 30 mg of high purity graphite were dispersed in 1 ml THF ultrasonically to form a black suspension. Four microlitres of this black suspension was pipetted directly on the freshly polished surface of glassy carbon electrode (GCE), forming M(SALEN)/Y composite film. Dried subsequently in air at room temperature for approximately 1 h, the composite film was further coated by 10 μl of polystyrene solution in THF solution (8 g/l) and then dried overnight at room temperature. Thus, the M(SALEN)/Y/GC modified electrode was obtained. Similarly, the MnY/GC modified electrode was obtained by replacing M(SALEN)/Y with MnY Zeolite. The graphite/GCE was prepared using only high purity graphite as the modifier by above approach. The M(SALEN)/Y/GCE, MnY/GCE, graphite/GCE and bare GCE were all used for working electrode in electrochemical experiments.

2.4. Apparatus and procedure

Electrochemical experiments were performed on a CHI model 600B (Shanghai, China) electrochemical workstation with a three-electrode system: bare GCEs or modified GCEs, working electrode; Pt plate (2 mm × 7 mm), counter electrode; saturated calomel electrode (SCE), reference electrode. The glassy carbon electrodes (geometric area, 0.0707 cm^2) were purchased from LK Co. (Tianjin, China). The buffer solution used was 0.025 mol l^{-1} Na_2HPO_4–0.025 mol l^{-1} NaH_2PO_4 (pH 6.90, 15 °C). Electrochemical experiments were performed in a one-compartment cell closed with a Teflon cap, through which the electrodes and gas bubbling system were fitted. High purity O_2 and N_2 regulated by two flowmeters (equipped with needle valves) were used to maintain dioxygen saturation and deoxygenate in the measurement cell.

Voltammetric experiments on M(SALEN)/Y modified electrodes were performed in phosphate buffer solution of pH 6.90. The buffer was purged with highly purified nitrogen for approximately 15 min before experiments. A nitrogen environment was then kept over solutions in the cell during the electrochemical experiments of M(SALEN)/Y. In the experiments of electrocatalytic reduction of dioxygen, O_2 was bubbled for 15 min before recording the voltammograms and chronocoulometric responses. All experiments were done at ambient temperature of 15 ±1 °C.

3. Results and discussion

3.1. Electrochemical behavior and stability of the M(SALEN)/Y/GCEs

The electrochemical behavior of M(SALEN)/Y/GCEs (M = Fe, Mn, Co) was studied by using cyclic voltammetry. Fig. 1 shows the cyclic voltammograms corresponding to the response of Mn(SALEN)/Y modified electrodes in a DMSO N_2-saturated solution containing 0.1 mol l^{-1} TBAP as supporting electrolyte. The curves of CV exhibit nearly symmetric anodic and cathodic peaks, corresponding to the Mn(III)/Mn(II) couple. The ΔE_p ($E_{pa} - E_{pc}$) values increase with increasing scan rate, but the formal potential ($E^{o\prime} = 1/2(E_{pc} + E_{pa}) = -0.295$ V) is almost constant, indicating the occurrence of quasi-reversibility of the electron transfer process [27,57]. The inset shows that the anodic and cathodic peak currents are linearly dependent on the scan rate in the range of 50–100 mV s^{-1}, implying the electrochemical characteristic of the surface-confined redox reactant rather than the freely diffusing species [58–60]. The value of $E^{o\prime}(-0.295$ V) of the electroactive species on the surface of Mn(SALEN)/Y/GCE is in line with the result reported by Fethi Bedioui's group [51] in same solution system, in despite of using different method for preparing modified electrodes. The Fe(SALEN)/Y and Co(SALEN)/Y modified electrodes have the similar result, with the formal potential of 0.245 V and 0.020 V being attributed to the well-known couple of Fe(III)/Fe(II) and Co(III)/Co(II), respectively, in the same electrochemically experimental conditions (not showed).

According to the Γ–Q relationship [30,60], the average surface coverage of electroactive species (Γ) can be evaluated from the equation $\Gamma = Q/nFA$, where Q is the charge obtained by integrating the cathodic peak under the background correction (at a low scan rate of 20 mV s^{-1}) and other symbols have their usual meanings. In the present case, the calculated values of Γ are 4.75×10^{-9}, 3.77×10^{-9} and 3.89×10^{-9} mol cm^{-2} for the Mn(SALEN), Fe(SALEN) and Co(SALEN) on the modified electrodes, respectively, which represent the amount of electroactive substance on the zeolite deposited on the electrode surface. The results show the amounts of electroactive molecules in the M(SALEN)/Y are very close. But it is important that the electroactivity of the three complexes in Y zeolite is different each other for oxygen reduction like that described in the following text.

The stability of the modified electrodes of Mn(SALEN)/Y/GCE was also examined by performing cyclic voltammograms of 50 repetitive cycles at scan rate of 50 mV s^{-1} in pH = 6.90 buffer solution saturated with O_2. As shown in Fig. 2, there were only slight changes in the peak current and the peak potential. On the other hand, the reproducibility of the Co(SALEN)/Y/GCE was also investigated by CVs in N_2- and O_2-saturated pH 6.90 buffer solution (more than 50 cycles). After immersing for 24 h the modified electrode in the same solution (pH 6.90), CV was carried out again in N_2-saturated solution and compared with the initial CV obtained under the same conditions. As shown in Fig. 3, the composite film of Co(SALEN)/Y/GCE was found to be well reproducibility. Thus the stability and the reproducibility of the modified electrodes used for electrocatalytic studies were established.

3.2. Electrocatalytic reduction of O_2 at M(SALEN)/Y/GCEs

The electrocatalysis of M(SALEN)/Y (M = Mn, Fe, Co) for dioxygen reduction at the modified electrodes was investigated by cyclic voltammetry. Typically, Fig. 4 shows the cyclic voltammograms of the Mn(SALEN)/Y/GCE in TBAP–DMSO solution saturated with N_2 (a) or oxygenated for 30 s (b), 150 s (c), 330 s (d) and 900 s (e) separately. As shown in Fig. 4, there is an increase in cathodic peak current with increasing oxygen bubbling time into the buffer solution. It was suggested that these cathodic waves enhancing with the increase in concentration of O_2 can be assigned to the O_2 reduction wave on the surface of the Mn(SALEN)/Y/GCE in aqueous solution. Compared with the cycle of Fig. 4a in the deaired solution, the cathodic peak currents of those waves of Fig. 4b–e in the presence of O_2 greatly increased whereas the anodic peak currents disappeared in the reverse scan since Mn(II)(SALEN) had reacted with oxygen. This implies that the oxygen reduction process taking place at the Mn(SALEN)/Y/GCEs is a typical catalytic reaction. Similar results were obtained from the electrodes adsorbing Fe(SALEN)/Y or Co(SALEN)/Y composite film.

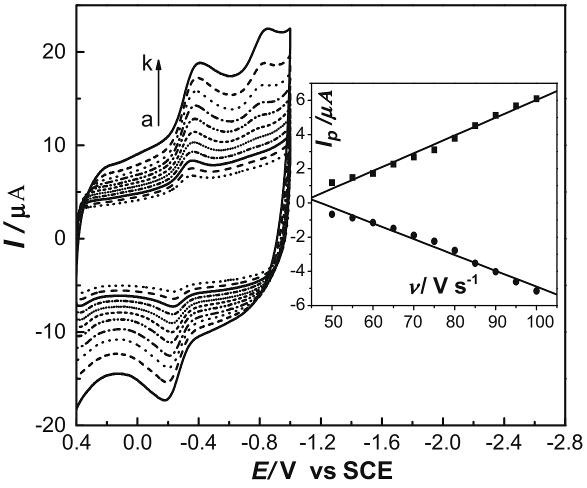

Fig. 1. CVs of the Mn(SALEN)/Y/GCE in N_2-saturated DMSO solution containing 0.1 M TBAP at scan rates: (a) 50, (b) 55, (c) 60, (d) 65, (e) 70, (f) 75, (g) 80, (h) 85, (i) 90, (j) 95, and (k) 100 mV s^{-1}. The inset shows plots of the cathodic and anodic peak current versus scan rate.

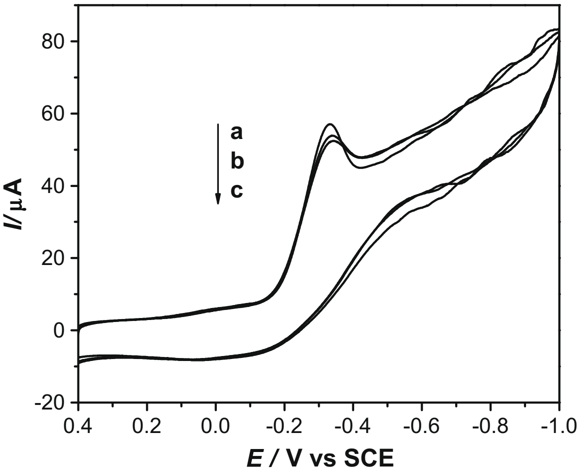

Fig. 2. CVs of the Mn(SALEN)/Y/GC modified electrode in O_2-saturated pH = 6.90 buffer solution. Curves (a), (b) and (c) correspond to the 1st, 2nd and 50th potential scans at 50 mV s^{-1}.

Fig. 5 displays cyclic voltammgrams of the Mn(SALEN)/Y/GCE in presence of N_2 (curve a) or saturated with O_2 (curve d). In the presence of N_2, a redox couple occurs at the formal potential of *ca.* −0.295 V (curve a) and its cathodic and anodic peak potential are observed at −0.357 V and −0.232 V, respectively, at a scan rate of 50 mV s^{-1}. With the presence of O_2 (saturated) in the buffer solution (pH 6.90), the cathodic wave is observed at the potential of *ca.* −0.333 V, close to the cathodic peak potential in the presence of N_2 (*ca.* −0.357 V in curve a). Also, the cathodic peak current

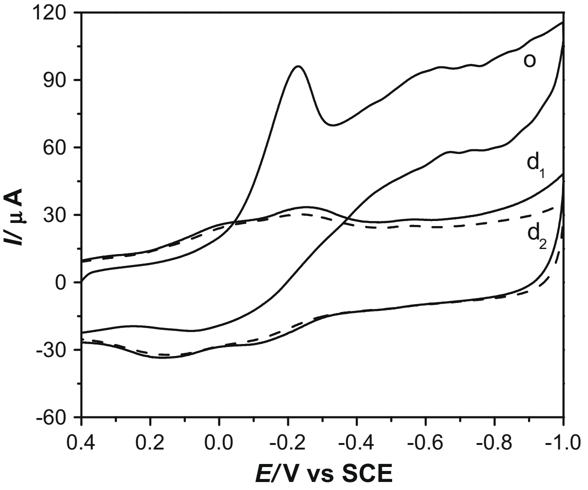

Fig. 3. CVs of the Co(SALEN)/Y/GCE in pH 6.90 buffer solution (o) O_2-saturated, (d_1) initial N_2-saturated, and (d_2) again N_2-saturated after scanning under N_2 and O_2-saturated and then keeping in pH 6.90 buffer solution for 24 h. Scan rate: 50 mV s^{-1}.

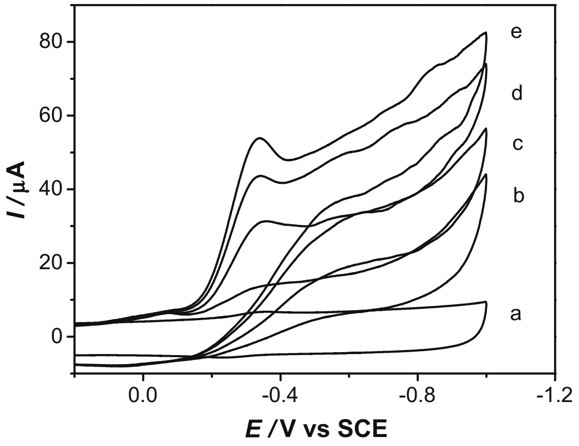

Fig. 4. CVs of Mn(SALEN)/Y/GCE at 50 mV s^{-1} (a) in 0.1 mol l^{-1} TBAP of DMSO N_2-saturated solution and (b–e) in 0.025 mol l^{-1} pH 6.90 buffer solution of increasing concentrations of O_2. The oxygenation time is: (b) 30 s; (c) 150 s; (d) 330 s; (e) 900 s.

increased greatly whereas the anodic peak current almost disappeared because of the presence of O_2, suggesting a typical characteristic of catalytic reduction reaction. Furthermore, the peak potential of curve d (*ca.* −0.333 V) on Mn(SALEN)/Y/GCE shifted towards the less negative direction with respect to that on the bare GCE (*ca.* −0.730 V, curve b) and the MnY/GCE (*ca.* −0.526 V, curve c). Namely, the overpotential required for O_2 reduction on the Mn(SALEN)/Y/GCE decreased by 397 and 193 mV compared with that on the bare GCE (b) and MnY/GCE (c), and higher peak currents was measured for Mn(SALEN)/Y/GCE than for bare GCE (b) or MnY/GCE (curve c). From above results, it can be concluded that the Mn(SALEN)/Y/GCE exhibits efficient electrocatalytic activity for the reduction reaction of O_2. Similar results were obtained for Fe(SALEN)/Y and Co(SALEN)/Y modified electrodes (see Fig. 6).

Fig. 6 shows cyclic voltammgrams of electrocatalytic O_2 reduction in the buffer solution (pH 6.90) at modified electrodes of Mn(SALEN)/Y/GCE (curve c), Fe(SALEN)/Y/GCE (curve d), Co(SALEN)/Y/GCE (curve e) as well as bare GCE (curve a) and pure graphite/GCE (curve b). The reduction peak potentials of waves (c)–(e) all shifted towards less negative direction compared with waves (a)

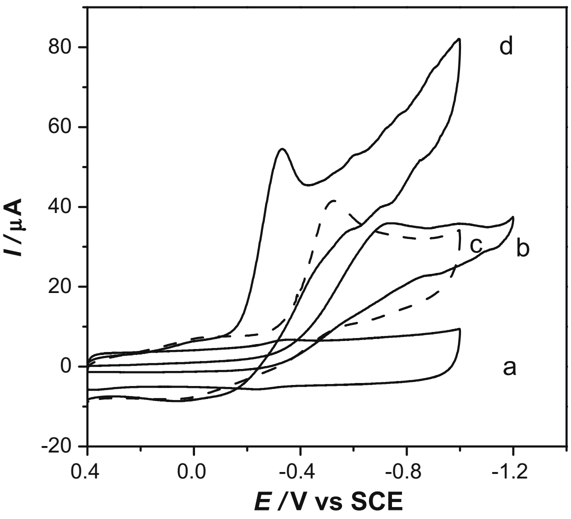

Fig. 5. CVs of Mn(SALEN)/Y/GCE (a) in 0.1 M TBAP of DMSO N_2-saturated solution and (d) in O_2-saturated pH 6.90 phosphate buffer solution. And CVs of (b) bare GCE and (c) MnY/GCE in the same conditions of (d) as reference. (Scan rate: 50 mV s^{-1}.)

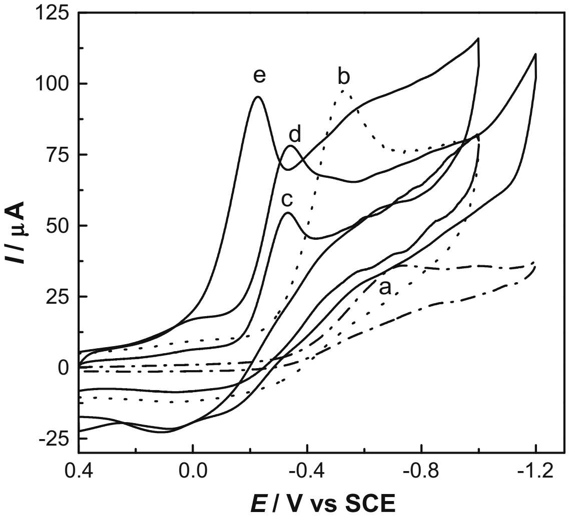

Fig. 6. CVs of (a) bare GCE, (b) graphite/GCE, (c) Mn(SALEN)/Y/GCE, (d) Fe(SALEN)/Y/GCE, and (e) Co(SALEN)/Y/GCE in O_2-saturated pH 6.90 buffer solution with. Scan rate: 50 mV s^{-1}.

and (b), and higher peak currents are observed relative to wave (a). Exactly, the overpotentials for oxygen reduction process decreased by 397, 393 and 505 mV on the Mn(SALEN)/Y, Fe(SALEN)/Y and Co(SALEN)/Y modified electrodes, respectively, relative to the bare GCE (curve a), and by 197, 193 and 305 mV relative to graphite/GCE (curve b). These results are clear indications for the occurrence of electrocatalytic reduction oxygen processes. Co(SALEN)/Y modified electrode is the most active electrocatalyst among the three M(SALEN)/Y (M = Mn, Fe, Co) modified electrodes.

3.3. The effect of scan rates on O_2 reduction at modified GCEs

Molecular oxygen may be reduced at the modified electrodes by a two-electron process to H_2O_2 or via a four-electron reduction to H_2O. How many electrons are involved in O_2 reduction? The cyclic voltammetric experiments at different scan rates (10–100 mV s^{-1}) were carried out in the potential window of −1.0 to 0.4 V versus

SCE. The results obtained from these experiments show that the peak currents of oxygen reduction on all M(SALEN)/Y/GCEs (M = Mn, Fe, Co) increased with increasing scan rate. The typical CVs of Co(SALEN)/Y/GCE in O_2-saturated pH 6.90 buffer solution recorded at various scan rates are shown in Fig. 7. The fact that there were only cathodic peaks and no anodic peaks suggests that the oxygen reduction process electrocatalyzed by the Co(SALEN)/Y/GCE is an irreversible reaction. In addition, the plots of reduction peak currents (i_p) versus the square root of scan rate ($\upsilon^{1/2}$) on the glassy carbon electrode modified with Mn(SALEN)/Y, Fe(SALEN)/Y and Co(SALEN)/Y are given in Fig. 8. The linearity of i_p–$\upsilon^{1/2}$ indicates that the electrocatalytic O_2 reduction process is controlled by O_2 diffusion. In the irreversible and diffusion-controlled case, the relationships of the peak current (i_p) and the peak potential (E_p) from cyclic voltammetry with scan rate (υ) are given as follows [61]:

$$i_p = 0.4958nFAc_0\left(\frac{\alpha n_a F}{RT}\right)^{1/2}\upsilon^{1/2}D_0^{1/2} \tag{1}$$

$$E_p = -\frac{RT}{2\alpha n_\alpha F}\ln\upsilon + A \tag{2}$$

$$A = E^{0'} - \frac{RT}{\alpha n_\alpha F}\left(0.78 + \frac{1}{2}\ln\frac{\alpha n_\alpha FD}{RTk^{0^2}}\right) \tag{3}$$

where i_p, n, α, n_α, A, c_0, D_0, υ represent the peak current, the total number of electrons transferred, the transfer coefficient, the apparent number of electrons transferred in the rate-determining step, the electrode area (0.0707 cm^2), the bulk concentration of dioxygen (1.25 mmol l^{-1} [62] used here), the oxygen diffusion coefficient (2.1×10^{-5} $cm^2\ s^{-1}$ [62] used here) and the scan rate, respectively; E_p, $E^{o\prime}$ and k^0 represent peak potential, the formal potential of the O_2 reduction process in volts and exchange rate constant in cm s^{-1}, respectively, other symbols have their usual significance. As shown in Fig. 8, the O_2 reduction peak currents at the Co(SALEN)/Y/GCE are the largest among these three different M(SALEN)/Y/GCEs (M = Mn, Fe, Co), and the slope of the straight line of i_p–$\upsilon^{1/2}$ obtained at the Co(SALEN)/Y/GCEs is slightly larger than those obtained at the other two modified electrodes. This suggests again that the Co(SALEN)/Y is most active electrocatalyst to oxygen reduction in present conditions.

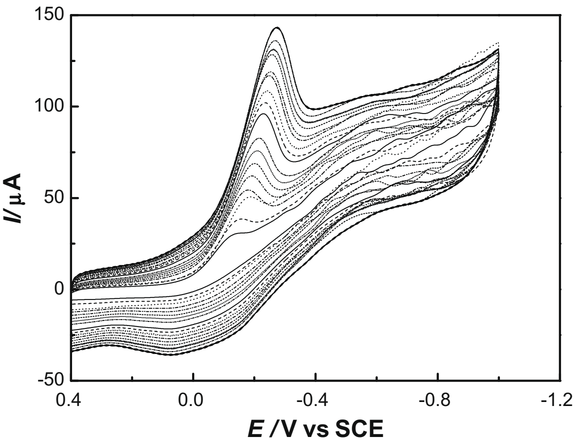

Fig. 7. CVs of the Co(SALEN)/Y/GCE in O_2-saturated pH 6.90 buffer solution at different scan rates. The scan rates are 10, 15, 20, 25, 30, 35, 40, 45, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100 mV s^{-1} from the inner to the outer curve.

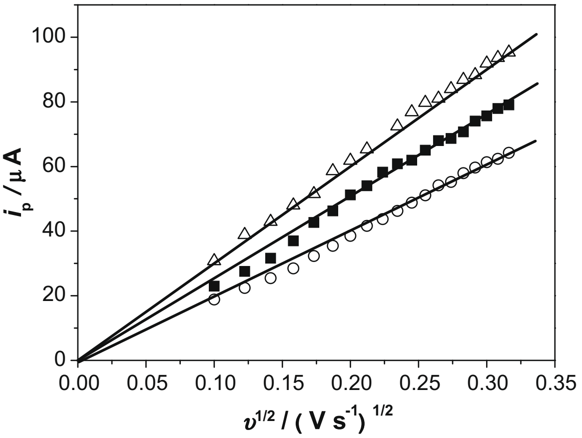

Fig. 8. Plots of reduction peak currents (i_p) versus the square root of scan rate ($\upsilon^{1/2}$) obtained from CVs on GCEs modified with (○) Mn(SALEN)/Y, (■) Fe(SALEN)/Y and (△) Co(SALEN)/Y. The scan rates are the same as those in Fig. 7.

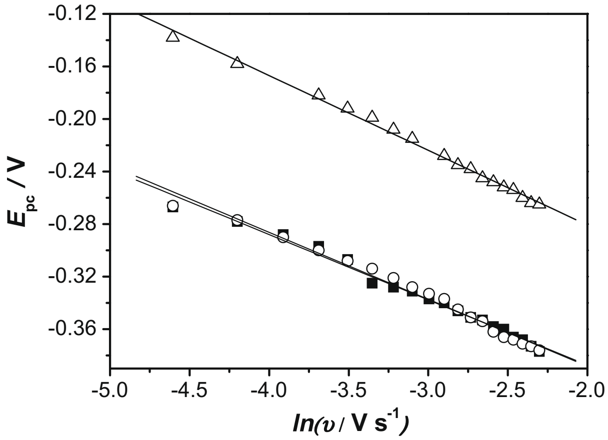

Fig. 9. Plots of E_{pc} versus ln υ obtained from CVs on GCEs modified with (○) Mn(SALEN)/Y, (■) Fe(SALEN)/Y and (△) Co(SALEN)/Y. The scan rates are the same as those in Fig. 7.

The dependence of E_p of oxygen reduction reaction on ln υ is shown in Fig. 9. The results indicate that the peak potentials for catalytic O_2 reduction at different scan rates shifted to more negative potentials with increase in scan rates. It is also seen from Fig. 9 that O_2 reduction peak potentials at the Fe(SALEN)/Y/GCE were close to those at Mn(SALEN)/Y/GCE, whereas the Co(SALEN)/Y catalyzed the oxygen reduction process at lower overpotential than the Fe(SALEN)/Y and Mn(SALEN)/Y. According to these linear plots of E_p versus ln υ, Tafel slopes of −50.97 mV, −49.71 mV and −56.91 mV are obtained for Mn(SALEN)/Y, Fe(SALEN)/Y and Co(SALEN)/Y, respectively. Thus, the calculated values of αn_α for Mn(SALEN)/Y, Fe(SALEN)/Y and Co(SALEN)/Y modified electrodes are 0.24, 0.25 and 0.22, respectively. With these αn_α values, the number of electrons transferred (n) for the O_2 reduction can be calculated as 3.48 for Mn(SALEN)/Y, 4.06 for Fe(SALEN)/Y and 4.93 for Co(SALEN)/Y, the both of the former are close to four electrons. This result suggests that O_2 reaching the electrode by diffusion is reduced electrochemically via a four-electron process to produce H_2O rather than two-electron step to H_2O_2. The reaction mechanism occurred on the M(SALEN)/Y/GCEs may include three steps as below (E1CE2 or E1CE2′):

$$\mathrm{SalenM(III)H_2O + e \rightleftharpoons SalenM(II)H_2O} \quad (\mathrm{E1}, n_1 = 1);$$

$$\mathrm{SalemM(II)(H_2O) + O_2 \rightleftharpoons SalenM(III)O_2 + H_2O} \quad (\mathrm{C});$$

$$\mathrm{SalenM(II)O_2 + 4H^+ + 3e \rightarrow SalenM(III)(H_2O) + H_2O} \quad (\mathrm{E2}, n_2 = 3);$$

$$\mathrm{SalenM(III)O_2 + 4H^+ + 4e \rightarrow SalenM(III)(H_2O) + H_2O} \quad (\mathrm{E2}', n_2 = 4)$$

The total number electrons transferred (n) on the electrode are the sum of n_1 for equation (E1) and n_2 for equation (E2 or E2′). When the oxygen reduction reaction occurred on the modified electrodes complied with the E1CE2 mechanism, the total number electrons are four, then five for E1CE2′. According to the n value based on cyclic voltammetry and chronocoulometry, the oxygen reduction reaction on the Mn(SALEN)/Y/GCE ($n = 3.48$ from CV, $n = 3.56$ from CC) and Fe(SALEN)/Y/GCE ($n = 4.06$ from CV, $n = 4.54$ from CC) can be ascribed to four-electron process, while that on Co(SALEN)/Y/GCE ($n = 4.93$ from CV, $n = 5.14$ from CC) may be attributed to five electrons process. But both of the mechanism has the same result: oxygen was electrochemically reduced into water on the M(SALEN)/Y/GCEs.

Accordingly, it can be concluded that M(SALEN)/Y (M = Mn, Fe, Co) in this system is a kind of good electrocatalysts for oxygen reduction reaction, which corroborates the results from thermodynamic calculations by Ma and Balbuena [63]. Fuerte et al. [53] and his group reported that CoTPP and FeTPP complexes supported onto MCM-41 and ITQ-6 were good electrocatalysts for ORR by two-electron process. According to Kadish et al. [64], two key points are important for estimating the quality of a catalyst for O_2 reduction. One point, also the more obvious, is the number of electrons, which should be close to 4.0 for producing H_2O rather than close to 2.0 for forming H_2O_2, and another point is the potential of O_2 catalytic reduction. The smaller the absolute value of O_2 reduction potential is, the more favorable the ORR will become.

3.4. Chronocoulometric studies

The chronocoulometric behaviors of the M(SALEN)/Y/GCEs (M = Mn, Fe, Co) are studied in the absence and presence of oxygen using the double potential-step technique. The initial and final potentials are 0.1 V and −0.4 V for Mn(SALEN)/Y/GCE, 0.4 V and −0.4 V for Fe(SALEN)/Y/GCE, 0.2 V and −0.3 V for Co(SALEN)/Y/GCE, respectively. As typical example, chronocoulometric curves of the Fe(SALEN)/Y/GCE are presented in Fig. 10. When the potential was reversed, a flat line appeared in the presence of oxygen. This proves that oxygen reduction is an irreversible reaction as reported by other groups [25,33,62]. As shown in Fig. 10, the direct reduction of O_2 at the bare GC electrode shows only residual charge, whereas the charge integrated from transient current at the Fe(SALEN)/Y/GCE seems to be large because of the catalytic effect of Fe(SALEN)/Y adsorbed composite film on the surface of glassy carbon on O_2 reduction. Also the electrochemical behavior of the Fe(SALEN)/Y/GCE shows reversible nature under N_2-saturated conditions but irreversible nature in the presence of oxygen because of the lack of anodic reaction. This indicates that the oxygen reduction reaction electrocatalyzed by the Fe(SALEN)/Y is an irreversibly electrocatalytic process. Q_{net} was determined by point-to-point subtraction of the forward charge found for the bare glassy carbon electrode from that for the Fe(SALEN)/Y/GCE in the presence of dioxygen. After the subtraction of the background charge, the plot of Q against t is converted into the plot of Q_{net} against $t^{1/2}$. In Fig. 11 and its inset, it is obvious that the charge (Q_{net}) has linear relationship with the square roots of time ($t^{1/2}$) for the oxygen reduction. The number of electrons involved in dioxygen reduction is determined from the slope of the Q_{net}–$t^{1/2}$, which was resulted from the chronocoulometric experiments carried out at the M(SALEN)/Y/GCE in the presence of O_2 using the Cottrell equation:

$$Q = 2nFAcD^{1/2}\pi^{-1/2}t^{1/2} \tag{4}$$

where F is Faraday constant, A is the electrode area, c is the concentration of dioxygen in high purity O_2-saturated solution, D is the diffusion coefficient of dioxygen in aqueous solution. Other symbols have their usual significance. With $A = 0.0707\ \mathrm{cm^2}$, $c = 1.25\ \mathrm{mmol\ l^{-1}}$ [62], slopes of $156.95\ \mu\mathrm{C\ s^{-1/2}}$, $200.38\ \mu\mathrm{C\ s^{-1/2}}$ and $216.88\ \mu\mathrm{C\ s^{-1/2}}$ are obtained from Eq. (4) for Mn(SALEN)/Y, Fe(SALEN)/Y and Co(SALEN)/Y modified electrode, respectively. On the assumption that the value of D is also $2.1 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ [62], the number of electron involved in oxygen reduction on Mn(SALEN)/Y/GCE, Fe(SALEN)/Y/GCE and Co(SALEN)/Y/GCE are calculated to be 3.56, 4.54 and 5.14, respectively. These results are closed to those from cyclic voltammetric experiment. Therefore, it is concluded again that the product of O_2 reduction on these three different M(SALEN)/Y/GC modified electrodes all should be water.

As shown in Fig. 12, the charge found for Co(SALEN)/Y/GCE is the largest while that for Mn(SALEN)/Y/GC modified electrode the lest. It is consistent with the result obtained from cyclic voltammetry. The number of electrons transferred in oxygen reduction on the M(SALEN)/Y/GCE (M = Mn, Fe, Co) from different electrochemical methods is summarized in Table 1.

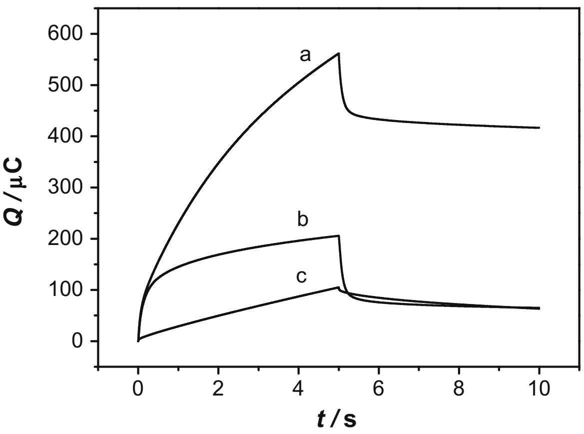

Fig. 10. Chronocoulomograms of the Fe(SALEN)/Y/GCE in pH 6.90 buffer solution in (a) presence of oxygen, (b) absence of oxygen, and (c) bare GC electrode in O_2-saturated buffer solution. And pulse width is 5 s.

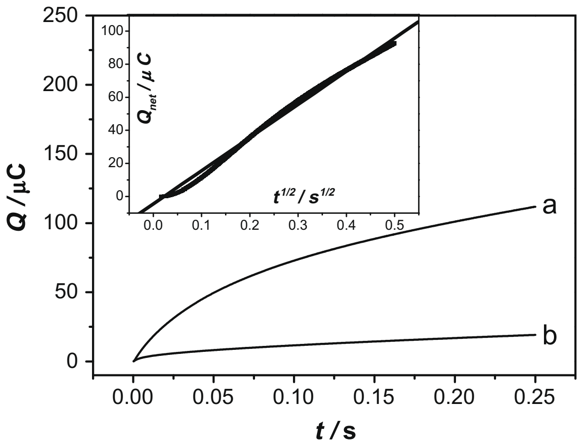

Fig. 11. Chronocoulomograms of O_2 reduction at (a) the Fe(SALEN)/Y/GCE and (b) the bare GCE in O_2-saturated pH = 6.90 buffer solution. The inset shows the plot of Q_{net}–$t^{1/2}$. Pulse width: 0.25 s.

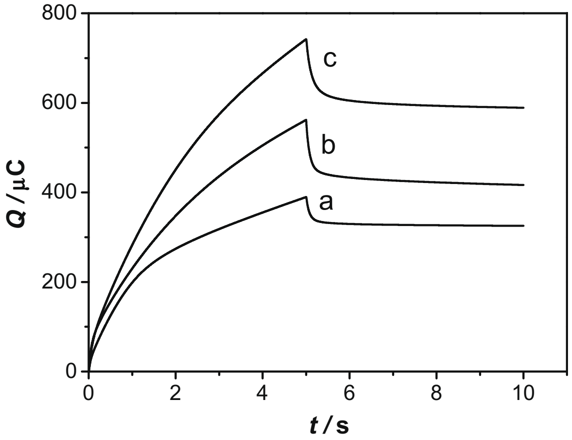

Fig. 12. Chronocoulomograms on (a) Mn(SALEN)/Y/GCE, (b) Fe(SALEN)/Y/GCE, and (c) Co(SALEN)/Y/GCE in O_2-saturated pH 6.90 buffer solution. And pulse width is 5 s.

Table 1
The number of electrons transferred in oxygen reduction process on the M(SALEN)/Y/GCEs (M = Mn, Fe, Co) as determined from different electrochemical techniques in pH 6.90 buffer solution.

Experimental methods	n (the total number of electrons transferred of O_2 reduction)		
	Mn(SALEN)/Y	Fe(SALEN)/Y	Co(SALEN)/Y
Cyclic voltammetry	3.48	4.06	4.93
Chronocoulometry	3.56	4.54	5.14

Dinuclear porphyrins [38,65,66] and polymeric metal Schiff-base complexes [44] showed good activity for the four-electron reduction of oxygen to water. The precise geometry of cofacial diporphyrins is a crucial factor that determines whether two- or four-electron reduction of dioxygen occurs [38,66]. Only appropriate interplanar distance to hold O_2 makes the two metal atoms act in concert to bind and reduce dioxygen in the gap between the porphyrin rings so as to realize a four-electron reduction of O_2. Zhou et al. [66] found that the diamido chain in $CoPP_0$ complex is too rigid to make the two porphyrins form "face-to-face" geometry, whereas the diamido-aliphatic chains in $CoPP_2$, $CoPP_5$ and $CoPP_8$ complexes are too flexible to constrain the porphyrins to a true "face-to-face" geometry. Bruice et al. [67] found that bis-cobalt porphyrin dimers for bis(5,10,15,20-tetraphenylporphyrin)s complexes with appropriate interplanar distances and high field N–H chemical shifts catalyze the reduction of dioxygen mainly through the $4e^-$ pathway, whereas those with long interplanar distances and low field N–H chemical shifts do so via a $2e^-$ path. According to Jiang and Kucernak [44], the microenvironment around the iron center in nonheme iron complexes could regulate O_2 activation. In the present investigation, metallosalen complexes included inside the Y zeolite cavity keep their initial geometric structure of neat complexes [8], the distance between the two neighboring M(SALEN) molecules inside the supercage of Y zeolite may be adapted to accommodate an oxygen molecule, which favors the concerted coordination of the dioxygen molecule to the metal ions of metallosalen. Also the encapsulated M(SALEN) complexes may have an appropriate microenvironment around the metal center allowing the four-electron reduction of molecular oxygen. Additionally, the present results clearly show that encapsulated Co(SALEN) complex is the most efficient catalyst for ORR, which is in accordance with the catalytic reaction results of oxidation of cyclooctane by M(SALEN)/NaX with dioxygen as oxidant by Haber group [5]. The activity of Mn(SALEN) for O_2 reduction is a little higher than that of Fe(SALEN) because the overpotential of O_2 reduction on the Mn(SALEN)/Y/GCE is a little lower than that on the Fe(SALEN)/Y/GCE. But the peak current of O_2 reduction on Fe(SALEN)/Y/GCE is higher than that on Mn(SALEN)/Y/GCE at the same conditions. In fact, there is no significant difference in catalytic activity of Mn(SALEN) and Fe(SALEN), which can be substantiated by other studies [1,5].

4. Conclusion

In this study, we prepared a stable modified electrode using the NaY-encapsulated metal (Mn, Fe, Co) SALEN complexes. These M(SALEN)/Y modified electrodes exhibited good electrochemical reproducibility and efficient electrocatalytic activity towards dioxygen reduction in present experimental conditions. The results clearly show that the Co(SALEN)/Y is the most active catalyst for oxygen reduction reaction. It is also demonstrated from cyclic voltammetric and chronocoulometric experiments that four or five electrons are involved in the dioxygen reduction process catalyzed electrochemically by the M(SALEN)/Y/GCEs. Moreover, 0.22–0.25 of the value of transfer coefficients for dioxygen reduction reaction on the M(SALEN)/Y/GCEs (M = Mn, Fe, Co) were determined by cyclic voltammetry. The M(SALEN)/Y/GCE could find potential applications in electroanalysis and electrochemical fields in virtue of many advantages of it such as easy fabrication and low cost. Further study is in progress on exploring applications of the NaY-encapsulated complexes modified GCEs as electrocatalysts and/or sensors. Catalytic activity and stability for the oxidation of methanol on the catalysts were studied by using cyclic voltammetry and chronoamperometry. The results will be published in other paper.

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