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Electrochemical Polymerization of Schiff Base Transition Metal Polymer Poly[Ni(Salen)] and Its Electrochemical Performance in Organic Electrolyte

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Poly[Ni(salen)] films were prepared by electrochemical polymerization with a constant potential method onto a polished Ti substrate in an organic electrolyte system. Fourier transform infrared spectroscopy (FTIR) was used to characterize the specific chemical groups of poly[Ni(salen)] and field emission scanning electron microscopy (FESEM) was used to analyze its morphology and microstructure. The electrochemical properties of poly[Ni(salen)] were investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) in 1 mol L^{-1} Et_3MeNBF_4/AN solution. Furthermore, the influence of different polymerization time on the microstructure and electrochemical performance were compared. The results showed that the surface coverage of poly[Ni(salen)] on the anode substrate increased as the polymerization time extension, but its electrochemical activity was greatly limited. The poly[Ni(salen)] film prepared in the polymerization time of 1000s showed the highest discharge specific capacitance (73.5 Fg^{-1}) at a low current density of 0.5 Ag^{-1}.

Keywords: Schiff base; Poly[Ni(salen)]; Electrochemical polymerization; Organic electrolyte

1. INTRODUCTION

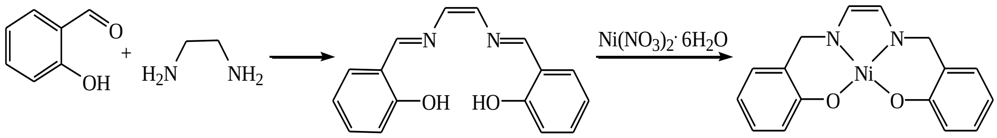
Schiff bases are the compounds with the azomethine group (-R=CN-) containing carbon, nitrogen and an aryl or alkyl group in their structures and can be synthesized via condensation of a primary amine with an active carbonyl compound [1]. In the recent decades, Schiff bases have attracted tremendous interests due to their unique properties and extensive applications in many scientific areas [2-4], e.g. anticancer and antibacterial [5-6], biosensor [7], catalysis [8], analytical chemistry [9-10] and corrosion prevention [11-12].

Transition metal complexes with Schiff bases, poly[M(Schiff)] (M=transition-metal), have the advantages of a wide potential window, redox conductivity and electron conductivity. This type of transition metal complexes can be polymerized onto the anodic electrode surface to form conductive films in solvents with low donor numbers [13]. A. Timonov discovered the unique properties of such conducting polymers in charge storage capacity and conducted a series of research using this kind of polymers as supercapacitor electrode materials [14-16].

In this paper, Poly[Ni(salen)] with N_2O_2 Schiff base ligand derived from salicyladehyde were electrochemically deposited onto a polished Ti substrate by a constant potential at 1.3V (*vs* Ag/AgCl) in an ethanol electrolyte, which was used as organic solvent in the electrochemical polymerization of poly[Ni(salen)] for the first time. Compared with other studies done in organic electrolytes such as acetonitrile [17-20], ethanol is non-toxic and much economic. In addition, the morphology, electrochemical properties and capacitance performance of the as-prepared Poly[Ni(salen)] films were also investigated.

2. EXPERIMENTAL

The Schiff base transition metal complexes monomer, Ni(salen), was synthesized according to the procedure in the literature [21] and then recrystallized from ethanol (>99.9%, A.R. grade). Scheme1 shows the synthesis scheme of Ni(salen).



Scheme 1. Synthesis scheme of Ni(salen).

The preparation of Schiff base transition metal poly[Ni(salen)] was in an organic electrolyte system, containing 8mL ethanol (>99.9%, A.R. grade), 4mM of Ni(salen) complexes monomer and 0.1M tetrabutylammonium perchlorate TBAP (>99%, A.R. grade). Ethanol was used as organic solvent in the electrochemical polymerization of poly[Ni(salen)] and TBAP acted as a network modifier, converting Ni(salen) into terminal ones thereby increasing the ionic conductivity. The poly[Ni(salen)] films were obtained via electrochemical deposition through a constant potential at 1.3V (*vs* Ag/AgCl) with a three-electrode configuration. A polished Ti substrate (1×2 cm) was used as working electrode, while a graphite rod (Φ1cm) as a counter electrode. After polymerization, the deposited electrode was taken out from the organic electrolyte, washed with ethanol and ultrapure water, and then dried in the air for further characterization.

The electrochemical properties of the as-prepared poly[Ni(salen)] films were investigated by cyclic voltammetry (CV, CHI 660e) and galvanostatic charge-discharge (GCD, CHI 660e) in a 1mol L^{-1} Et_3MeNBF_4/AN organic solution. These tests were carried out in a three-electrode cell using the as-prepared poly[Ni(salen)] working electrode, a graphite rod as the counter electrode and an Ag/AgCl reference electrode. The specific chemical groups of poly[Ni(salen)] were characterized by using Fourier transform infrared spectroscopy (FTIR, FTIR-8400S) and its morphologies by a field emission scanning electron microscope (FESEM, JEOL, JSM-6701F).

3. RESULTS AND DISCUSSION

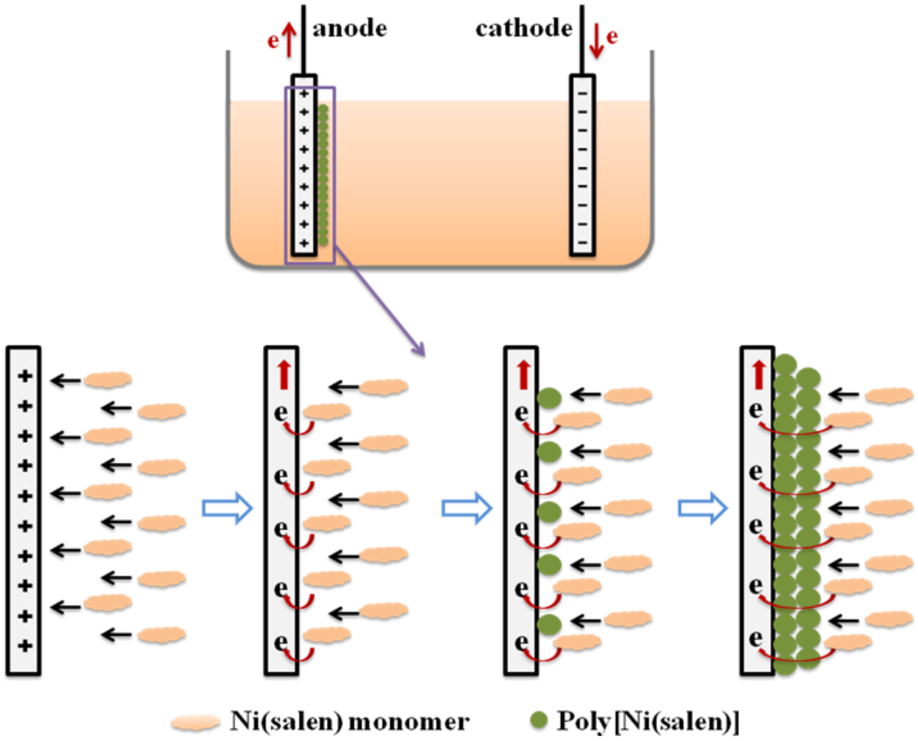


Figure 1. Scheme of the electrochemical polymerization process of poly[Ni(salen)] films.

Figure 1 shows the scheme of the electrochemical polymerization process of poly[Ni(salen)] films in the ethanol electrolyte system. It can be observed that the orange complexes monomer Ni(salen) dissolve completely and uniformly in ethanol. When a constant potential was given, the Ni(salen) monomers moved towards to the working electrode through electromigration. Once the Ni(salen) monomers collided with the electrode, they would be oxidized and then deposited onto the anodic electrode surface. Besides, with the rising of polymerization time, the thickness of dark green polymer films would also increase proportionally.

In order to obtain the FTIR sample, the dark green poly[Ni(salen)] films on the Ti substrate need to be scraped with a blade and then use these powders and KBr to make a tablet as the FTIR sample. Figure 2 shows the FTIR spectra of poly[Ni(salen)]. The broad absorption peak at around 3425.02cm^{-1} is assigned to the hydroxyl group (-OH) which is generally caused by absorbed water during the test. The weak bands around the range of 2990-2850 cm^{-1} and 2390-2280 cm^{-1} are in accordance with CH_n and nitrile respectively. The strong absorption peaks at 1618.11 cm^{-1}, 1446.83cm^{-1} and 1091.31cm^{-1} are characteristic of C=N stretch of the salen ligand, phenyl ring in-plane vibration and C-O stretch vibration respectively. These peaks in the range of 2000-500 cm^{-1} indicate the presence of poly[Ni(salen)] structure [22-23].

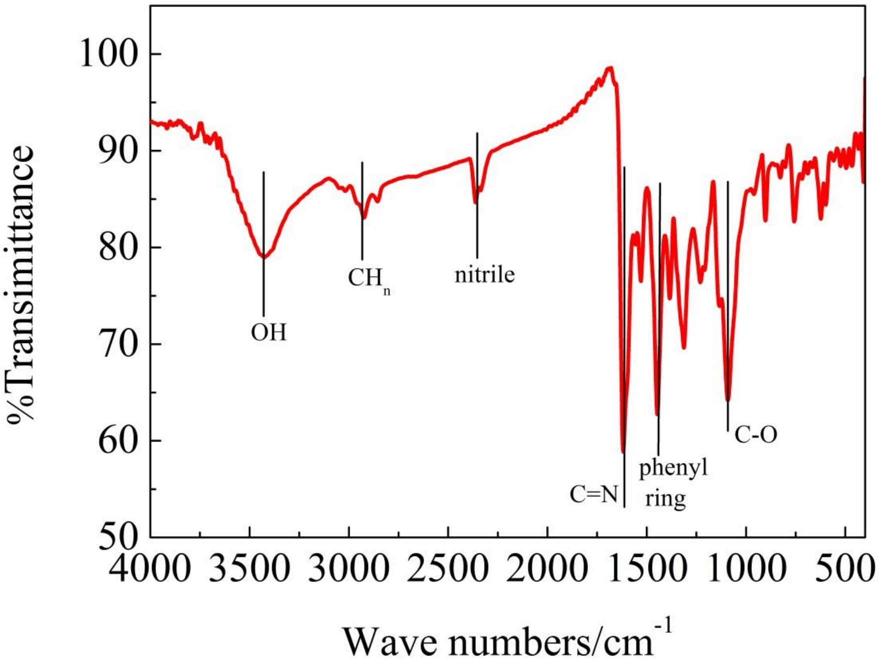


Figure 2. FTIR spectra of poly[Ni(salen)].

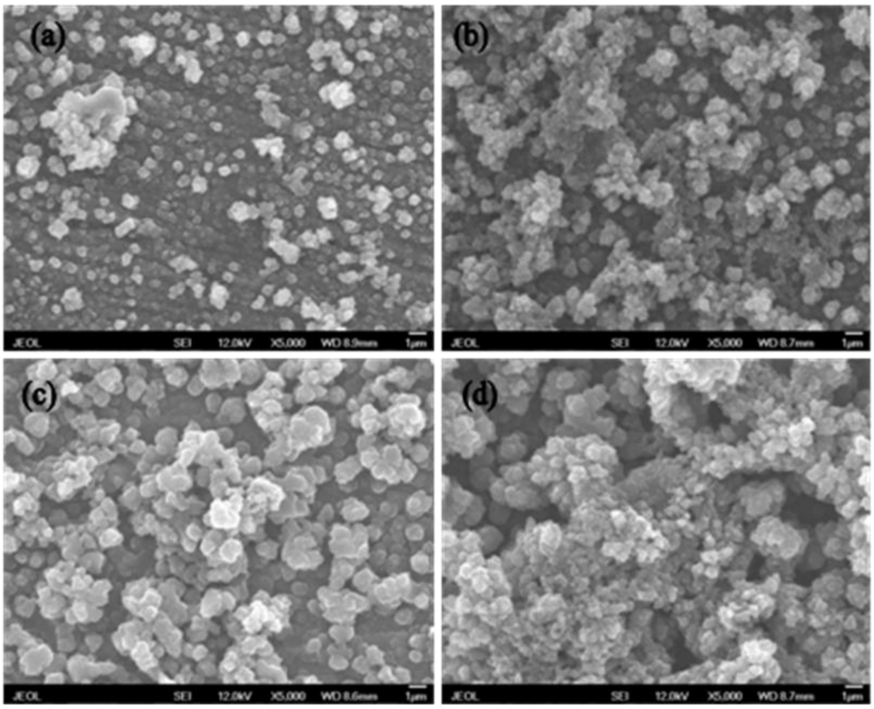


Figure 3. FESEM images of poly[Ni(salen)] film prepared in different polymerization time of (a) 1000s, (b) 2000s, (c) 3000s and (d) 4000s, respectively.

In the process of electropolymerization, the current density was very low at around 70μA cm^{-1}, mainly due to the limited conductivity. Thus, the mass of active material on the substrate electrode was relatively small, so the effect of polymerization time on the morphology and electrochemical performance of poly[Ni(salen)] was investigated. The corresponding FESEM images are showed in Figure 3 at a magnification of 5000 times. It is obvious to see that the poly[Ni(salen)] exhibit spherical particles and these particles uniformly distribute in the surface of the substrate electrode with few areas appearing agglomeration. Moreover, the surface coverage of poly[Ni(salen)] on the anode substrate and the film thickness increased significantly as the polymerization time extension from 1000s (Figure 3a) to 4000s (Figure 3d), and the size of the spherical poly[Ni(salen)] particles had some apparent changes, especially in Figure 3d, where the particle size became much smaller.

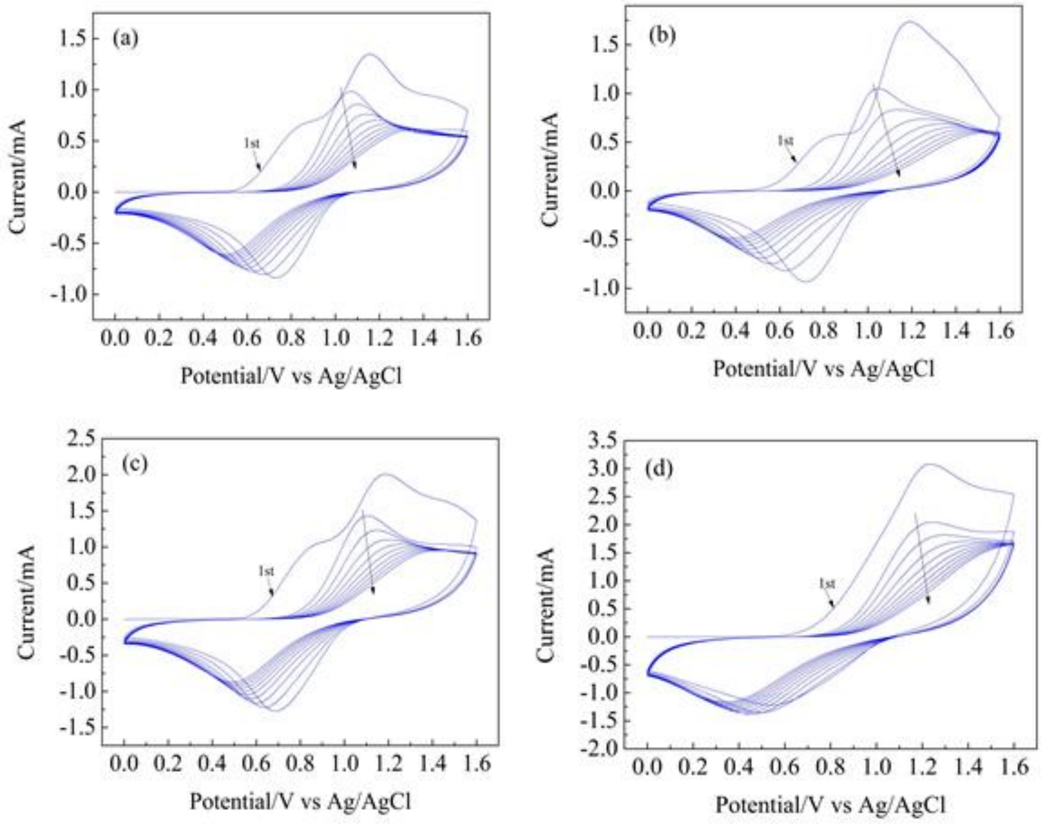


Figure 4. CV curves of poly[Ni(salen)] film prepared in different polymerization time of (a) 1000s, (b) 2000s, (c) 3000s and (d) 4000s respectively, at a rate of 50mVs^{-1} from 0-1.6V for 1st to 10th scans in 1mol L^{-1} Et_3MeNBF_4/AN.

Since the increase of polymerization time results in a rise of the mass of active material on the substrate electrode, it may lead to some changes in electrochemical performance for such conducting polymers. Therefore, subsequent cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests in 1 mol L^{-1} Et_3MeNBF_4/AN solution were carried out to study the effect of polymerization time on electrochemical performance of poly[Ni(salen)]. Figure 4 shows CV curves at a rate of 50 mVs^{-1} from 0-1.6 V for 1st to 10th scans of poly[Ni(salen)] film prepared in different polymerization time of

(a) 1000s, (b) 2000s, (c) 3000s and (d) 4000s, respectively. The first scan circle in every CV curve was quite different from others, indicating the presence of other irreversible reaction which would disappear in the next scans. Meanwhile, the redox peak current decreased gradually with the number of scan circle increasing, while the potential gap between oxidation peak and reduction peak broadened. These CV curves illustrated that this type of conducting polymer poly[Ni(salen)] showed the typical characteristics of pseudo-capacitance based on reversible faradic transitions, but the reversibility reduced with the poly[Ni(salen)] film thickness increasing.

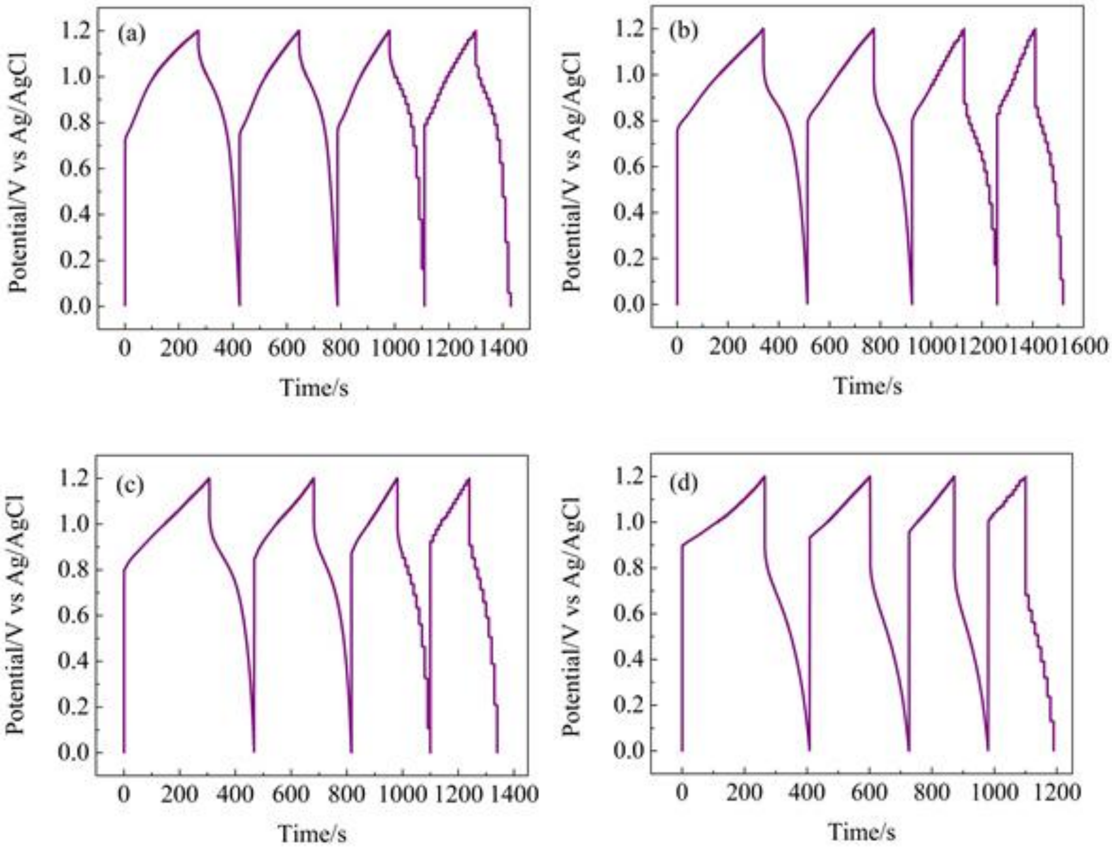


Figure 5. GCD curves of poly[Ni(salen)] film prepared in different polymerization time of (a) 1000s, (b) 2000s, (c) 3000s and (d) 4000s respectively, in 1mol L^{-1} Et_3MeNBF_4/AN.

The corresponding GCD curves are shown in Figure 5 as well. Tests were carried out at a charge-discharge current density of 0.5 Ag^{-1} with a potential window of 0-1.2V (*vs* Ag/AgCl). There were significant differences in these GCD curves. The potential was climbing rapidly from 0V to around 0.8V when giving a charging current every time. It should be an approximate linear line segment with a certain slope if the electrode material exhibits a character of electric double layer (EDL) capacitance. Thus, the conclusion that the poly[Ni(salen)] failed to show a electric double layer capacitance could be deduced. As to a supercapacitor material, the other type of energy storage mechanism is pseudo-process charge storage which is different from electric double layer (EDL) [24].

By analyzing the GCD curves, it could be noticed that the initial potential was higher from Figure 5(a) to Figure 5(d) at the charge stage when the poly[Ni(salen)] films were thicker, and the "IR-drop" was more obvious at the discharge stage. The non-linear potential increase from around 0.8V and decrease at the discharge stage indicated the presence of a redox reaction which gave rise to the pseudo-process energy storage. This point of view also could be supported by the obvious redox peak in the CV curves (Figure 4). From the GCD curves, it can be claimed that the pseudo-capacitance has a major contribution to the energy storage of the poly[Ni(salen)]. However, there was a downward trend in cycle time, therefore the cycle stability needed to be improved in future work. In addition, considering of the mass of the active material on the electrode, the poly[Ni(salen)] films prepared in 1000s had a relatively better electrochemical performance.

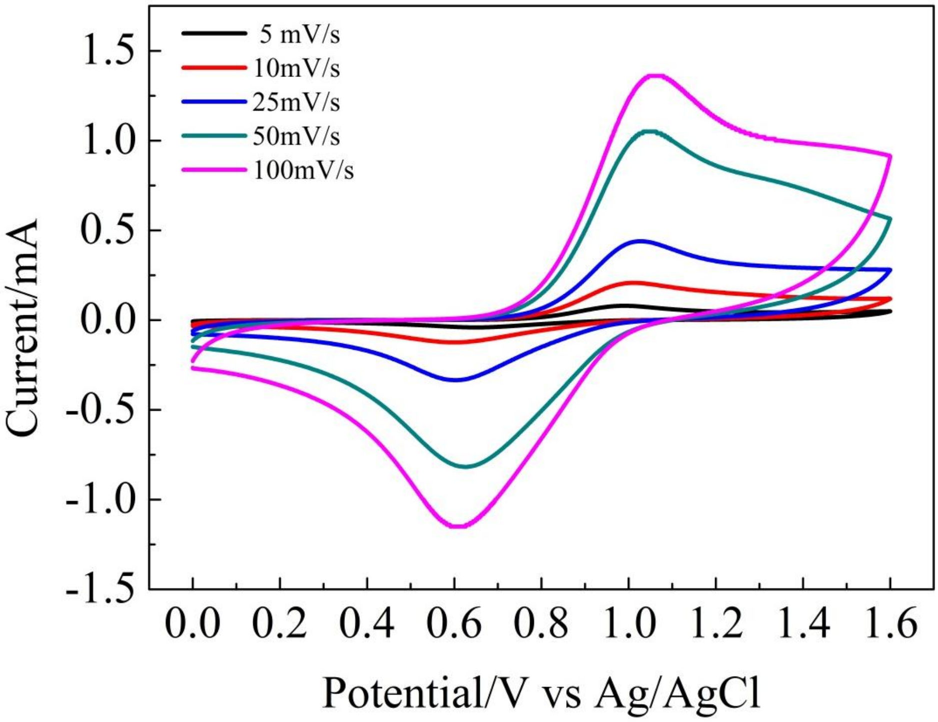


Figure 6. CV curves of poly[Ni(salen)] film at different scan rates in 1mol L^{-1} Et_3MeNBF_4/AN.

Pseudo-capacitance based on a reversible faradic transition of poly[Ni(salen)] prepared in 1000s was studied by cyclic voltammetry. The CV curves of poly[Ni(salen)] between the potential range of 0V and 1.6V vs the Ag/AgCl at different scan rate are showed in Figure 6. There is an obvious pair of redox peaks which are associated with a redox switching. The oxidation peak is approximately at 0.62V and the reduction peak at 1.02V. As the scan rate increasing from 5 mVs^{-1} to 100 mVs^{-1}, the current has a corresponding rise.

Galvanostatic charge-discharge tests were then used to evaluate the specific capacitance of the poly[Ni(salen)] films at different current densities with a potential window of 0-1.2V (*vs* Ag/AgCl). The specific capacitance can be calculated according to the formula below,

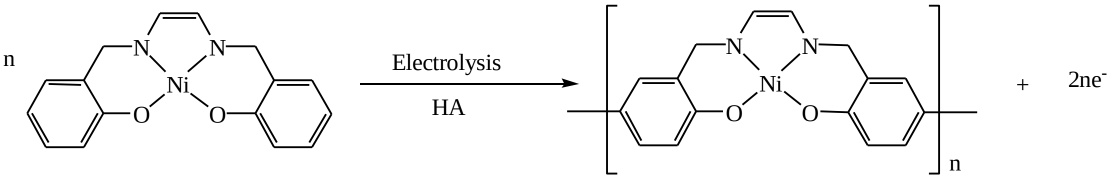
$$C_m = \frac{C}{m} = \frac{I \times t}{\Delta V \times m}$$

where C_m is specific capacitance [Fg^{-1}]; I is charge-discharge electric current; t is the discharge time; ΔV is 1.2 V in our tests, and m is the theoretical mass of active material on the substrate electrode.

The mass of the deposited poly[Ni(salen)] was calculated by Faraday's law according to the formula below, assuming the current efficiency is 100%,

$$m = \frac{Q \times M}{z \times F}$$

where m is the theoretical mass of the deposited poly[Ni(salen)]; Q is the charge loading; M is the molar mass of the Ni(salen) monomer which is 323.03 $gmol^{-1}$; F is the Faraday constant, and z is the number of electron transfer based on the reaction shown in Scheme 2:



Scheme 2. The electropolymerization reaction for synthesizing of poly[Ni(salen)].

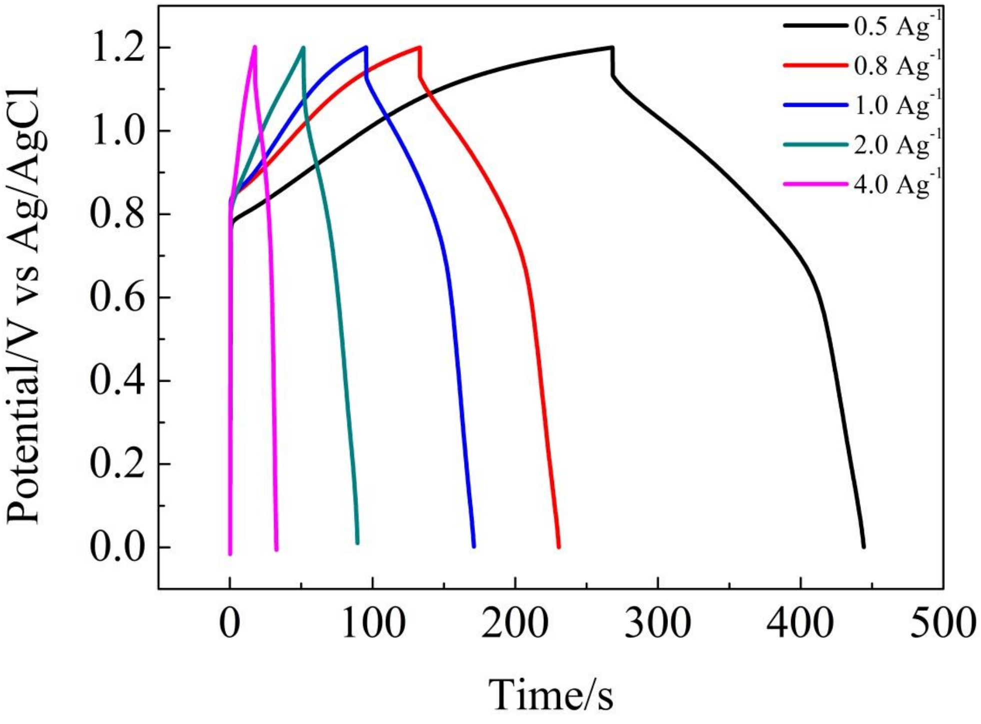


Figure 7. Galvanostatic charge-discharge curves of poly[Ni(salen)] film at different curent densities in 1mol L^{-1} Et_3MeNBF_4/AN.

Figure 7 shows the GCD test for poly[Ni(salen)] at different current densities in 1 molL^{-1} Et_3MeNBF_4/AN solution. There are two voltage stages in the range of 0-0.8V and 0.8-1.2V respectively. The first stage is associated to the electric double layer (EDL) capacitance and the second stage is ascribed to the pseudo-capacitance. The result of GCD tests shows that the highest specific capacitance is 73.5 Fg^{-1}, when the current density is at 0.5 Ag^{-1}. Due to the limited reversibility of the faradic transition and the minor contribution of electric double layer (EDL), the capacitance of the poly[Ni(salen)] needs to be improved in the further work when using it as the electrode material in a supercapacitor. However, by comparing with the Schiff base transition metal polymers [25-26], poly[Ni(salen)] shows a moderate performance at the same current density. In a word, as a novel type of conducting polymer, poly[Ni(salen)] has a wide potential range (0-1.2V) and a typical pseudo-capacitance property.

4. CONCLUSIONS

In summary, the poly[Ni(salen)] films were successfully prepared by electrochemical polymerization in an ethanol electrolyte system, which provides a new kind of organic electrolytes to synthesize poly[Ni(salen)]. Compared with other studies done in organic electrolytes such as acetonitrile, ethanol is much economic and non-toxic. The electrochemical tests investigated in 1 mol L^{-1} Et_3MeNBF_4/AN solution indicate that poly[Ni(salen)] is a kind of conducting polymers with the typical pseudo-capacitance property. Furthermore, polymerization time had obvious effects both on the morphology and the electrochemical performance of poly[Ni(salen)]. The extension of the polymerization time would lead to the surface coverage of poly[Ni(salen)] on the anode substrate increasing, but the electrochemical performance slipping down. The poly[Ni(salen)] film prepared in the polymerization time of 1000s reached the highest discharge specific capacitance at73.5 Fg^{-1}.

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