Effects of Potential Modes on Performances of Electrodeposited Poly[Ni(salen)]/MWCNTs Composite as Supercapacitor Electrode Material

Zhixun ZHU, Jian LU, Xiping LI, Guofeng XU, Cheng CHEN, and Jianling LI*

Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, No. 30 College Road, Beijing 100083, China
* Corresponding author: lijianling@ustb.edu.cn

ABSTRACT
In this investigation, poly[Ni(salen)]/MWCNTs composites (PMCs) were synthesised by electrodeposition method via linear sweep potential (LSP), potentiostatic (PS) and one-step potential pulse (SPP) modes, respectively. It was found that different modes resulted in diverse poly[Ni(salen)] morphologies. With the equal deposition time, the PMCs prepared via PS mode exhibited better capacity performances as electrode materials of supercapacitors. The specific capacitances of products prepared by LSP, PS and SPP modes were 72.8 F g\(^{-1}\), 151.5 F g\(^{-1}\) and 106.2 F g\(^{-1}\) at 0.02 mA cm\(^{-2}\), which is due to the difference of thickness of poly[Ni(salen)] wrapped on MWCNTs and length of poly[Ni(salen)] nano-belt. In addition, all the samples exhibited good reversibility as electrode materials.

Keywords : Poly[Ni(salen)]/MWCNTs Composites, Potential Mode, Electrodeposition, Supercapacitor

1. Introduction
Global climate change, limited fossil fuels resources, and energy security crisis have strongly warned us to develop endurable and environmentally energy storage technologies. In recent years, supercapacitors (SCs) have attracted significant attentions due to their higher power density, long life cycle and bridging function for the power/energy gap between traditional capacitors (which have high power output) and batteries/fuel cells (which have high energy storage).\(^1\,\,2\) It has been recognized that SCs is a potential energy storage device that stores normal or unstable energy and release a large current density within a short time interval. The charge storage mechanism of electrode materials can be divided into two categories: (i) electrical double-layer SCs, in which only pure physical charge accumulation occurs at the electrode/electrolyte interface and (ii) faradaic SCs, in which the electrode material is electrochemically active.\(^3\) Conducting polymers is an important faradaic electrode material with many advantages such as high voltage window, high reversibility, and so on. Transition metal complexes polymer with tetradentate N\(_2\)O\(_2\) Schiff-base ligand poly[N,N’-ethylenebis-(salicylaldimino) nickel(II)] (poly[Ni(salen)]) is a new class of novel macromolecular material that consists of organic and inorganic components, the molecular structure of Ni(salen) and polyNi(salen) are shown in Fig. 1. As an metal-containing polymers, poly[Ni(salen)] has an potential to be electrode materials which not only allowing fast, reversible faradaic reactions (redox reactions) taking place, but also can be conveniently polymerized by direct electrosynthesis.\(^4\,\,5\)

Carbon nanotubes (CNTs) are attractive materials as their superb properties such as unique network of mesopores, high electrochemically accessible surface area of porous nanotubes arrays, excellent electronic conductivity and useful chemical stability.\(^6\,\,\,7\) By combining MWCNTs and poly[Ni(salen)], the electron, proton conduction and specific surface area of the formed composite are facilitated. The deposition of polymer will be improved as well. Electrodepositing poly[Ni(salen)] on MWCNTs has some advantages such as high efficiency, easy operation and more available operational parameters on growth. Gao et al have prepared fascicular and ferroconcrete-like poly[Ni(salen)] by cyclic voltammetry mode.\(^8\,\,\,9\) Belt and particle microstructures of poly[Ni(salen)] were synthesised by Zhang et al.\(^10\,\,\,11\) However, potential modes have played a vital role in electrodeposition and strongly acted on the morphologies and electrochemical performances of deposited materials.

In this article, we compared the effects of LSP, PS and SPP modes on electrodepositing poly[Ni(salen)]. The effects mainly include morphologies and electrochemical properties of composites, especially the specific capacitance. Additionally, the electrodeposited conditions of polymer by three modes and testing environment for corresponding composite electrodes are same.

2. Experimental
2.1 Materials
MWCNTs and acetonitrile (AN, >99.5%, A.R. grade) were purchased from Shenzhen Nanotech Port Co., Ltd. and Xilong Chemical Co., Ltd. respectively. Meanwhile, tetrabutylammonium perchlorate (TBAP, >99.9%, C.P. grade) from Zhong Sheng Hua Teng Co., Ltd. were used for preparing solution. 1 mol L\(^{-1}\) triethyl-methylammonium tetrafluoroborate (Et\(_3\)MeNBF\(_4\), >99.9%, C.P. grade) was testing electrolyte. The Ni(salen) monomer was prepared by chemical synthesis method in the literature.\(^12\) The MWCNTs electrode was fabricated by mixing MWCNTs in N-methyl-2-pyrrolidone (NMP) through sonication. Then the slurry was dropped on a cleaned titanium sheet (1 × 1 cm\(^2\)) with the coating mass of 0.1 mg.
cycles. Also, PS mode [Fig. 2(b)] and SPP mode [Fig. 2(c)] were discharge curves as follows:

measurements above were carried out on the VMP2 electrochemical with same counter and reference electrodes. All electrochemical trile. Cyclic voltammetry (CV), chronoamperometry, galvanostatic

3. Results and Discussion

the discharging time (s).

2.2 Preparation and instruments

The electrodeposition of Ni(salen) on the prepared MWCNTs electrode was happened in three-electrode system by VMP2 electrochemical workstation. The acetonitrile solution contains 1.0 mmol L\(^{-1}\) Ni(salen) monomer and 0.1 mol L\(^{-1}\) tetrabutylammonium perchlorate for electrodeposition. An activated carbon sheet and a capillary Ag/AgCl wire were utilized as the counter electrode and reference electrode, respectively. The PMCs prepared by LSP mode [Fig. 2(a)] labeled as SLSP. The sweep potential range of LSP mode was 0 to 1.2 V accompanying a sweep rate of 20 mV s\(^{-1}\) for 10 cycles. Also, PS mode [Fig. 2(b)] and SPP mode [Fig. 2(c)] were applied for preparing PMCs labeled as SPS and SPPP, respectively. The specific settings of those modes are: PS potential, electrodeposition time at 0.95 V for 10 min followed by relaxation time of 10 min at 0 V, and for SPP mode, pulse time of 20 s at 0.95 V followed by 30 s relaxation time and total 10 min of oxidative time. All potentials in the experiments are versus Ag/AgCl.

2.3 Characterization and calculation

The chemical composition and surface morphologies of MWCNTs and PMCs samples were characterized by Fourier transform infrared spectra (Shimadzu, FTIR-8400S), field emission scanning electron microscopy (FESEM, Zeiss Supra55 microscope) and transition electron microscopy (TEM, JEOL JEM 2011), respectively. The poly[Ni(salen)]/MWCNTs electrodes were tested in a non-monomer solution of 1.0 mol L\(^{-1}\) Et\(_3\)MeNBF\(_4\) in acetonitrile. Cyclic voltammetry (CV), chronoamperometry, galvanostatic charge/discharge tests were used to measure the PMCs electrodes with same counter and reference electrodes. All electrochemical measurements above were carried out on the VMP2 electrochemical workstation. The capacitance values (Cm) can be calculated from discharge curves as follows:

\[
C_m = \frac{It}{Vm}
\]

Where \( m \) is the mass of the electroactive materials on the electrodes (g), \( P \) is the potential range (V), \( I \) is current (mA), and \( t \) is the discharging time (s).

3. Results and Discussion

3.1 FTIR spectra characterization

Figure 3 shows the FTIR spectra of Ni(salen) monomers (SM), SLSP, SPS, SPPP, respectively. For Ni(salen) monomers, before electrochemical polymerization, it can be seen that the broad absorption band centered at 3440 cm\(^{-1}\) is attributable to the band –OH stretching vibrations due to the adsorption of water in open air.\(^{17}\) The bands in the range of 3000–2835 cm\(^{-1}\) is assigned to CH\(_2\), and the appearance of protons as a doublet is due to mutual coupling or a fluctuation behavior generated by (–CH\(_2\)H\(_2\)C–) moieties.\(^{18}\) Moreover, the C=N imine stretching band is observed at around 1632 cm\(^{-1}\).\(^{19}\) But the band at 1596 cm\(^{-1}\) is split by Fermi resonance, which is the result of mixing with the asymmetric stretching vibration of C=N=C absorption. As the dipole moment change of Ni-O is larger than Ni-N, the Ni-O stretching band is stronger than the Ni-N stretching band.\(^{20}\) At lower frequency, the composites exhibited bands around 680–560 cm\(^{-1}\) and 490–400 cm\(^{-1}\), which were assigned to Ni-N and Ni-O vibration modes, respectively.\(^{21}\) The three absorption peaks at 1540 cm\(^{-1}\), 1450 cm\(^{-1}\), 1350 cm\(^{-1}\) suggest that phenoxide bridging with the metal atom are existed,\(^{22,23}\) and peak 1090 cm\(^{-1}\) indicates the presence of C–O stretch vibrations. Similar to C=N imine stretching band, C–O is also split by Fermi resonance, which is assigned by peak 1120 cm\(^{-1}\). For all the PMCs electrodes (Fig. 3), to a large extent, the absorption band in range of 2900–4000 cm\(^{-1}\) is in accordance with Ni(salen) monomers. However, the absorption peaks of PMCs samples SLSP, SPS, SPPP (Fig. 3) at 1540 cm\(^{-1}\), 1450 cm\(^{-1}\), 1350 cm\(^{-1}\) and bands around 680–560 cm\(^{-1}\), 490–400 cm\(^{-1}\) are weakened or disappeared when compared with Ni(salen) monomers. And the absorption peaks and bands are characteristics of phenyl ring inplane vibrations and Ni-O, Ni-N stretch vibrations, respectively. Furthermore, the absorption peak at 2360 cm\(^{-1}\) represents the residual acetonitrile. Thus, it can be illustrated that the interaction between poly[Ni(salen)] and MWCNTs have hindered the vibrations of radicals. The appearances of absorption peaks in the band range of 3000–4000 cm\(^{-1}\) for SLSP, SPS, SPPP mean that the structure of composite has not been fractured.

3.2 FESEM and TEM images of MWCNTs and PMCs

Figure 4 shows the FESEM images of MWCNTs and PMCs with different potential applying modes: LSP, PS and SPP. The morphologies and inner structures were amply observed. As shown in Fig. 4(a), the tubular intertwist structure of MWCNTs, more clearly at enlarged views Fig. 4(b), is characteristic of plenty of spaces between single MWCNTs. For SLSP, SPS and SPPP samples, poly[Ni(salen)] was deposited on MWCNTs for two forms: around the nanotubes and bonding polymer upon the MWCNTs, but the poly[Ni(salen)] nano-belts on the surface of MWCNTs layer is different. Meanwhile, some subtle differences of nanotubes [Fig. 4(c)–(h)] were also observed. As seen in Fig. 4(c), (d), as more adhesive growth of poly[Ni(salen)], the tubes of composite sample SLSP is thicker than the pure MWCNTs. Some spaces between MWCNTs have become smaller or filled by the grown poly[Ni(salen)]. The surface of carbon nanotubes layer is covered by

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**Figure 2.** The applied potential modes of preparing PMCs: (a) LSP; (b) PS; (c) SPP, the total oxidative time of each potential mode is 10 min.

**Figure 3.** (Color online) FTIR spectra of samples: SM, SLSP, SPS, SPPP, SM (Ni(salen) monomers sample).

**Figure 4.** (Color online) FESEM images of MWCNTs and PMCs with different potential applying modes: LSP, PS and SPP.
intersecting nano belt-like polymer as well. While for sample SPS, (f), the tubular intertwist MWCNTS is just a little thicker than pure nanotubes but thinner than sample SLSSP. Sparse long nano-belt polymer is distributed on the surface of MWCNTS layer, as seen in Fig. 4(e). As with SSSP, as shown in Fig. 4(g), (h), the nano-belts polymer is approximately equal that looks like several cuts of long nano-belt from Fig. 4(f). The as-grown poly[Ni(salen)] coated multiwall carbon nanotubes being thicker tubes.

To further analyze the thickness of adhesive growth poly[Ni(salen)] in the PMCs, the TEM micrograph of carbon nanotubes was observed. As shown in Fig. 5, MWCNTs were wrapped by a polymer wall, and its thickness order for potential modes is SPP > LSP > SPP. The thickness of adhesive poly[Ni(salen)] electrodeposited by SPP potential mode is the thickest, and some site on tube can reach 4 nanometers.

From the FESEM and TEM images of SLSSP, SPS and SSSP samples, we can conclude that different potential modes lead to different electrodeposition results of poly[Ni(salen)]. The polymerization firstly happened on the surface of supported MWCNTs. That’s mainly because MWCNTs provide spaces for the growth of poly[Ni(salen)] as the concentration of monomer is high enough. But different potential modes may result in different changes of monomer concentration around nanotubes. The relaxation time of 30 s in SPP mode and low potential time in LSP mode provide enough time for the diffusion of monomers, whereas little diffusion time for the PS mode. So the adhesion poly[Ni(salen)] layer along MWCNTs deposited by SPP [Fig. 5(c)] and LSP [Fig. 5(a)] modes are much thicker than poly[Ni(salen)] layer with PS mode [Fig. 5(b)]. That means the thickness of polymer attached to nanotubes has close relation to relaxation time of potential modes. So the gaps between nanotubes in PMCs prepared by SPP and LSP modes have been severely stuffed. Moreover, the polymerization mode of transition metal complexes with tetradeinate N2O2 Schiff-base ligand is to form a chain structure through generating C–C bonds between the phenyl rings in ligands monomers. According to nucleation and growth theory of electrodeposition, if the rate of growth paralleling to the electrode surface is higher than the rate of vertical growth, the appearance structure of electrodeposition polymer is a strip. Thus, the Ni(salen) monomers were electrodeposited to be a nano belt-like polymers with a width about 100 nanometers. The length of the polymer chain can be dominated by the sustained time of potential electrodeposition, which can be confirmed from the FESEM images in Fig. 4.

The microstructure of PMCs has a close relationship with the electrodeposition mode, specifically, the applied potential pattern and time. Under the liner sweep potential, massive polymers deposited along the MWCNTs and nano belt-like polymer grows upon the MWCNTs layer. That’s because the periodic voltage change provides enough time for monomer molecule diffusion. In contrast, the sustained high potential results in little polymer electrodeposited along MWCNTs and most for the long belt-like poly[Ni(salen)] beyond the MWCNTs layer. This structure is beneficial to keep the gap between nanotubes and good electrolyte ions diffusion, so the space clogging is the smallest. For SPP mode, MWCNTs was coated with a thick polymer-wall and short nano belt-like poly[Ni(salen)] cuts covered the MWCNTs layer. In addition, the cuts of poly[Ni(salen)] belt were caused by the time of sustained high potential polymerization, more specifically, only 20 seconds sustained one pulse. Similar to LSP mode, enough time for monomer molecules diffusion followed by a great amount of poly[Ni(salen)] grown around the nanotubes.

3.3 Electrochemical characterization

The typical cyclic voltammograms of different PMCs electrodes with a potential window from 0 to 1.2 V (vs. AgCl/Ag) are shown in Fig. 6. The CV showed that the current responses of composites increased a little based on MWCNTs electrode at low potential. This illustrated that poly[Ni(salen)] also produced electric double layer capacitor for composite electrode. Therefore, both of MWCNTs and poly[Ni(salen)] have contributed the electric double layer capacitor for composite electrode. The current response of composites largely increased at high potential meaning that the redox reaction of electrodeposited poly[Ni(salen)] contributed large pseudocapacitance and much larger than double layer capacitor. The reversible transition between the neutral state and oxidation state of poly[Ni(salen)] results in a couple of symmetrical peaks in the current responses of PMCs and facilitate pseudocapacitance supplement. The oxidation and deoxidization peaks in a potential window between 0.6 V and 1.2 V arrived in CV curves of PMCs indicate that the electrochemical activity of grown poly[Ni(salen)] in composites is good. The following corresponding Ni^{3+/2+} redox process, which shows the majority capacitance of poly[Ni(salen)] is provided by the center metal Ni.

\[
poly[Ni(salen)] + nBF_4^{-1} \leftrightarrow poly[Ni(salen)]ox(BF_4)_n + ne^{-}
\]
Meanwhile, it can be observed that current response peaks of PMCs in the order of SPS > SLSP > SSPP. Obviously, current response of SPS is the highest reaching more than 5 times of SSPP which may be caused by the different availability of poly[Ni(salen)] in composites. The fundamental data of peaks in cyclic voltammograms were shown in Table 1. Potential differences of current responses peaks are all below 0.1 V. The mass of PMCs are nearly with the same electrodeposition time. However, the contact with electrolyte was interfered with thickly and disorderly accumulated nano-belts polymer cuts and intersecting nano belt-like polymer in SSPP and interfered with thickly and disorderly accumulated nano-belts electrodeposition time. However, the contact with electrolyte was interfered with thickly and disorderly accumulated nano-belts polymer cuts and intersecting nano belt-like polymer in SSPP and SSPP, SSPP electrodes at a sweep rate of 100 mV s⁻¹. The mass of PMCs are nearly with the same electrochemical reaction. The current response of SPS is also higher than SLSP and SSPP electrode. Otherwise, the potentials of oxidation peaks of three kinds of PMCs electrodes are close to 0.95 V which corresponds to the settings of electrochemical deposition potential.

The galvanostatic charge/discharge is an important test to measure the capacitive behavior of electrode materials. Figure 7 shows the measured curves of PMCs and MWCNTs electrodes at the current density of 0.02 mA cm⁻². All curves have shown a symmetric shape. The maximum discharge time of PMCs electrode reaches more than 5 times of MWCNTs electrode. The discharge curves of PMCs electrodes can be obviously divided into two parts: (i) at low potential region (0–0.6 V), the poly[Ni(salen)] is in electrochemical inert zone and discharge plots exhibit a nearly straight line shape that indicates the good electrochemical double-layer capacitive behavior of PMCs electrodes. Owing to the charge adsorption of polymers, the double layer capacity of PMCs is a little larger than that of MWCNTs based on the CV curves. (ii) When the potential reach 0.6 V, the electrochemical activity of poly[Ni(salen)] begin to increase, neutral state translates to oxidation state to store energy called pseudocapacitance. So the discharge curves of PMCs become gentle in region 0.6–1.2 V. We know that the energy stored by pseudocapacitance largely exceeds double layer capacitance. Therefore, the poly[Ni(salen)] utilization is a vital component for the capacitive behavior of PMCs electrodes. The electrochemical active area (EAA) of electrodes including MWCNTs, SLSP, SPS, and SSSP were calculated from constant potential step method. The EAAs of PMCs and MWCNTs electrodes by potential transformation (0–1.2 V) have been shown in Table 2. The values of PMCs are all higher than MWCNTs for SLSP and SSPP electrodes at a sweep rate of 100 mV s⁻¹. Table 2. The electrochemical active area (EAA) of electrodes including MWCNTs, SLSP, SPS, and SSSP.

<table>
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<th>composites</th>
<th>Epc/V</th>
<th>Epc/V</th>
<th>Jpc/A cm²</th>
<th>ΔE/V</th>
<th>m/mg</th>
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</thead>
<tbody>
<tr>
<td>SLSP</td>
<td>0.941</td>
<td>0.864</td>
<td>2.47</td>
<td>0.077</td>
<td>0.1965</td>
</tr>
<tr>
<td>SPS</td>
<td>0.935</td>
<td>0.851</td>
<td>2.85</td>
<td>0.084</td>
<td>0.1407</td>
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<tr>
<td>SSPP</td>
<td>0.954</td>
<td>0.902</td>
<td>1.50</td>
<td>0.052</td>
<td>0.1362</td>
</tr>
</tbody>
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Figure 6. (Color online) Cyclic voltammograms curves of MWCNTs, SLSP, SPS, SSSP electrodes at a sweep rate of 100 mV s⁻¹.

Table 1. The cyclic voltammograms data at a sweep rate of 100 mV s⁻¹ and active material mass for SLSP, SPS, SSSP electrodes.

Figure 7. (Color online) Galvanostatic discharge plots of MWCNTs, SLSP, SPS, SSSP electrodes with a current density of 0.02 mA cm⁻².

Figure 8. (Color online) The specific capacitances of MWCNTs, Poly[Ni(salen)] in composites, SLSP, SPS, SSSP electrodes versus discharging current densities.
The specific capacitance at different current densities was calculated from galvanostatic discharge test for the MWCNTs support electrode and PMCs electrodes. Figure 8(a) shows the different specific capacitance of poly[Ni(salen)] in composites in the order of $S_{PS} > S_{SPP} > S_{SLP}$. The same order also arise for composites electrodes shown in Fig. 8(b). The specific capacitances of poly[Ni(salen)] are 151.5 F g$^{-1}$, 106.2 F g$^{-1}$ and 72.8 F g$^{-1}$ at a current density of 0.02 mA cm$^{-2}$ for samples $S_{PS}$, $S_{SLP}$ and $S_{SPP}$, respectively. That means poly[Ni(salen)] in $S_{PS}$ electrode was more fully used. So we conclude that the sparse long nano-belts polymer and the maintained gaps of $S_{PS}$ facilitate the contact between active materials and electrolyte and result in high electrochemical active area. As a result, the orders that occurred in current responses of CV, EAA and capacitance of poly[Ni(salen)] in composites showed that the PMCs electrodeposited by PS mode with the sparse nano-belts and spaces microstructure possess better electrochemical performances.

4. Conclusion

Poly[Ni(salen)}/MWCNTs composites synthesized by different modes exhibited distinct morphology and electrochemical performance. For LSP and SPP modes, cyclic variation of potential provides more time for the diffusion of monomer molecules, which results in more poly[Ni(salen)] polymerized on the surface of carbon nanotubes and less on the MWCNTs layer. On the contrary, the PS mode leads to the opposite phenomenon. For the part on the PS electrode MWCNTs layer was easier to contact with the electrolyte, the composites electrode prepared by PS mode expressed a higher utilization rate, which caused a higher capacity. In summary, PS is a better mode compared with LSP and SPP modes in electrodepositing poly[Ni(salen)}/${\text{\text{MWCNTs}}$ composite as electrode for SCs.

Acknowledgments

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References