



# Redox poly[Ni(saldMp)] modified activated carbon electrode in electrochemical supercapacitors

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## ABSTRACT

The complex (2,2-dimethyl-1,3-propanediaminebis(salicylideneaminato))–nickel(II), [Ni(saldMp)], was oxidatively electropolymerized on activated carbon (AC) electrode in acetonitrile solution. The poly[Ni(saldMp)] presented an incomplete coated film on the surface of carbon particles of AC electrode by field emission scanning electron microscopy. The electrochemical behaviors of poly[Ni(saldMp)] modified activated carbon (PAC) electrode were evaluated in different potential ranges by cyclic voltammetry. Counterions and solvent swelling mainly occurred up to 0.6 V for PAC electrode by the comparison of  $D^{1/2}C$  values calculated from chronoamperometry experiments. Both the Ohmic resistance and Faraday resistance of PAC electrode gradually approached to those of AC electrode when its potential was ranging from 1.2 V to 0.0 V. Galvanostatic charge/discharge experiments indicated that both the specific capacitance and energy density were effectively improved by the reversible redox reaction of poly[Ni(saldMp)] film under the high current density up to  $10 \text{ mA cm}^{-2}$  for AC electrode. The specific capacitance of PAC electrode decreased during the first 50 cycles but thereafter it remained constant for the next 200 cycles. This study showed the redox polymer may be an attractive material in supercapacitors.

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## 1. Introduction

Electrochemical double-layer supercapacitors (EDLCs), due to its' outstanding power density and extremely long lifetime vs. lithium ion battery, are widely used as an auxiliary power source in electric vehicles and other electric devices [1]. However, the drawback of low energy density for activated carbon (AC) electrode significantly limits EDLCs' wide application. Incorporating some conducting polymers on top of porous activated carbon materials is one practical approach to compensate this shortcoming. Conducting polymers (e.g. polyaniline [2–4], polypyrrole [5,6], polythiophene and its derivatives [7–9]) have been investigated as active materials of supercapacitor, which have larger capacitance and higher energy density than activated carbon but faster decline of performance.

Most polymers which have been employed as the electroactive materials for supercapacitors are either p-doped or n-doped reversibility in aqueous solutions and nonaqueous systems. When p-doped (n-doped) electrochemically, electrons are removed from (injected onto) the polymer backbone through the external circuit, while anions (cations) from the electrolyte solution are incorporated into the polymer film to maintain overall charge neutrality

[10–12]. This makes the polymer susceptible to the attack of reactive species in the electrolyte solution, which may reduce the cycle life.

We noticed that one type of conducting polymer produced by electrooxidization of Ni(salen)-type monomer (see Chart 1) has the potential to be used as electroactive material of supercapacitors. Nickel(II) complexes with  $\text{N}_2\text{O}_2$  Schiff base ligands derived from salicylaldehyde have long been used as homogeneous electrocatalysts in the reduction of alkyl and aryl halides [13–15]. Oxidation of these nickel(II) complexes can lead to polymerization on the conducting electrode surfaces and generate electroactive films in moderate/weak donor solvents [16–19]. The polymerization of Ni(salen)-type monomers has been reported by several groups. Those studies have focused on the electropolymerization process, polymer structure, and identification of the redox couples [20–25].

Ni(salen) species are characteristic of square planar or nearly planar in steric orientation [26–28]. In the process of the electrooxidization of Ni(salen)(II)-type monomers, the oxidized species react with each other to form a stack structure [21], meanwhile, charge-compensating counterions in the electrolyte penetrate into the polymer so as to provide electroneutrality (processes that like p-doped and d-doped).

The polymer films produced by Ni[salen]-type monomers may be combined with porous activated carbon materials to improve the performance of EDLC capacitors (specific capacitance, energy density, etc.). In this paper, we prepared the poly[Ni(saldMp)](3)-

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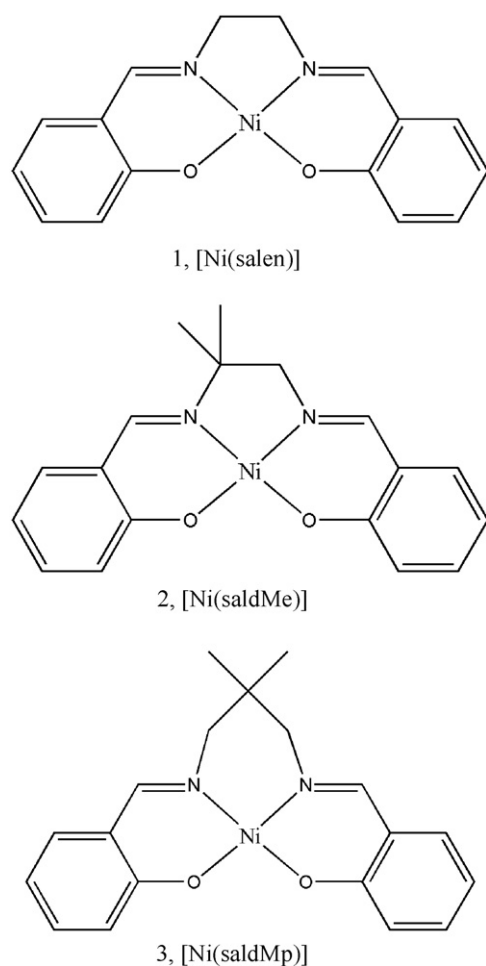


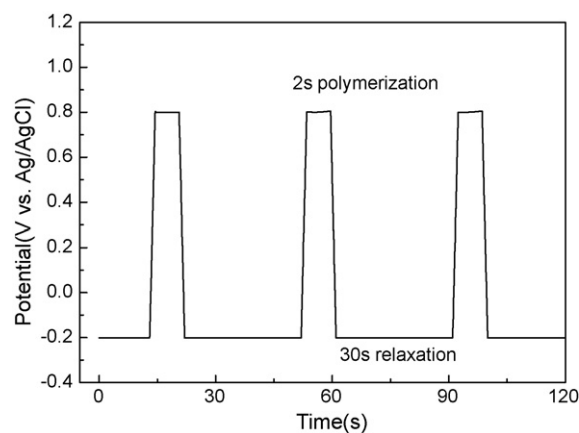
Chart 1. Structure of some typical Ni[salen]-type monomers.

modified AC electrode by a two-step potential pulse procedure and reported the characterization of PAC electrode through cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry. The morphology of PAC electrode was characterized via field emission scanning electron microscopy. Finally, the galvanostatic charge/discharge tests were conducted in order to evaluate the stability of poly[Ni(saldMp)] as an electroactive material in electrochemical supercapacitor.

## 2. Experimental

### 2.1. Materials

Acetonitrile (AN, >99.9%, A.R. grade) was purchased from Guangdong Xilong Chemical Co., Ltd. Tetrabutylammonium perchlorate (TBAP, >99.9%, C.P. grade) and triethylmethylammonium tetrafluoroborate ( $\text{Et}_3\text{MeNBF}_4$ , >99.9%, C.P. grade) were purchased from ZhongShengHuaTeng Co., Ltd. 2,2-Dimethyl-1,3-propanediamine (dMp, >97%, G.C.T) was purchased from J&KChemica Co., Ltd. They were used as received. The complex Ni(saldMp) monomer (2,2-dimethyl-1,3-propanediaminebis(salicylideneaminato))-nickel(II) was synthesized following the procedure in the literature and recrystallized from acetonitrile [29]. Results from CHN elemental analysis were in agreement with the expected theoretical composition for  $\text{Ni}(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2) = 367.07 \text{ g mol}^{-1}$ . Anal. Calc.: C, 62.17; H, 5.49; N, 7.63. Found: C, 62.52; H, 5.56; N, 7.94%.



Scheme 1. The two-step potential pulse procedure.

Activated carbon was purchased from Kuraray Chemical Co. Ltd, with BET surface area around  $1683 \text{ m}^2 \text{ g}^{-1}$ . The AC electrode was prepared by mixing the activated carbon with polyvinylidene fluoride (PVDF) and commercial carbon black (80:10:10 wt%) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on a 20- $\mu\text{m}$ -thick Al foil (current collector) with the coating thickness of 100  $\mu\text{m}$ .

### 2.2. Poly[Ni(saldMp)] film electropolymerization on graphite and AC electrode

Linear sweep potential method was used for the preparation of poly[Ni(saldMp)] on the graphite electrode: the sweep potential ranged from 0.0 V to 1.2 V, and the sweep rate was set to  $10 \text{ mV s}^{-1}$  for the total of 10 cycles. A two-step potential pulse step procedure (Scheme 1) was used for the preparation of poly[Ni(saldMp)]-modified AC electrode (PAC): 2 s pulse time at 0.8 V followed by 30 s relaxation time at 0.0 V, for the total of 250 cycles. There is a limitation of diffusion rate for the monomer molecules and electrolyte in the solution during the electrochemical polymerization occurs on AC electrode due to the large surface area and highly porous structure of the activated carbon. Based on this consideration, the two-step potential pulse step procedure was adopted to polymerize a thin polymer film on carbon grains of AC electrode. During the short pulse step (2 s) of the procedure, the monomers nearby the surface of carbon grains are electrooxidized and deposit on the surface. During the subsequent relaxation step (30 s) of the procedure, the monomers locating in the bulk of electrolyte solution diffuse into the inner of the AC electrode so that the monomer molecules which were exhausted in preceding pulse can be compensated and electrooxidized in the next step.

The electropolymerization was conducted in a closed three-electrode compartment cell. The working electrodes were polished graphite electrode ( $\Phi = 1 \text{ cm}$ ), or 100- $\mu\text{m}$ -thick activated carbon electrode ( $1 \text{ cm} \times 1 \text{ cm}$ ), an AC electrode with  $8 \text{ cm}^2$  surface area as the counter electrode and a capillary Ag|AgCl wire as the reference electrode (all potentials here are given vs. Ag|AgCl) [30,31]. The polymerization solution was made with acetonitrile, 0.1 mM complex Ni(saldMp) monomer, and 0.1 M TBAP. The poly[Ni(saldMp)] and PAC electrodes were then washed in acetonitrile in order to remove any soluble species from the film and were tested in a monomer-free solution of 1 M  $\text{Et}_3\text{MeNBF}_4$  in acetonitrile.

Apparent surface coverage ( $\Gamma_{\text{app}}$ ,  $\text{mol cm}^{-2}$ ) was calculated using the equation  $\Gamma_{\text{app}} = \Delta Q/nFA$ , where  $n$  is the number of transferred electrons,  $F$  is the Faraday's constant,  $A$  is the area of AC electrode in  $\text{cm}^2$ , and  $\Delta Q$  is the charge (area) difference under the

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