

Carbon Nanotubes Chemically Modified by Metal Phthalocyanines with Excellent Electrocatalytic Activity to Li/SOCl₂ Battery

Yan Gao,^a Siwen Li,^a Xiao Wang,^a Ronglan Zhang,^a Gai Zhang,^b Ying Zheng,^c and Jianshe Zhao^{a,z}

^aKey Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, People's Republic of China ^bSchool of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710021, People's Republic of China ^cDepartment of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

Carbon nanotubes (CNTs)-templated metal phthalocyanines (MPc) (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II)) assemblies (CNTs-CONH-MPc) were synthesized and characterized by IR, XRD, SEM, XPS. The lithium-thionyl chloride (Li/SOCl₂) cells using CNTs-CONH-MPc as catalysts showed excellent performance, which the capacities increased by 15.44-88.49%, and the initial voltages improved to 3.09-3.22 V. The sequence of the electrochemical catalytic performance of CNTs-CONH-MPc was ranked by central metal ion: Co > Ni > Mn > Fe > Cu > Zn. Based on cyclic voltammetry measurements, the reasonable mechanism is proposed and the role of catalyst is verified. The modified CNTs by MPc greatly promoted the electronic transmission, which significantly improved the performance and the initial voltage of Li/SOCl₂ battery. © 2017 The Electrochemical Society. [DOI: 10.1149/2.0611706jes] All rights reserved.

Manuscript submitted December 28, 2016; revised manuscript received February 21, 2017. Published March 31, 2017.

In the 1970s, thionyl chloride battery as a new type of efficient chemical power causes the wide attention of scientific research workers. Li/SOCl₂ battery possesses several prominent characteristics such as high specific energy, high voltage and low temperature performance as well as long life in the storage, which makes this type of batteries exclusive in some extreme conditions.¹ Due to its many unique characteristics, Li/SOCl₂ battery is widely applied in petroleum mining, sea exploration and consumer industry.^{2,3} However, one of limitations of Li/SOCl₂ battery is that the actual voltage value is far less than the theory value (3.65 V). Extensive works have been done to increase the practical energy of Li/SOCl₂ battery by adding catalysts into electrolyte.4-8

Carbon nanotubes (CNTs), a new carbon derivatives, possess high specific surface, prominent electrical conductivities and unique chemical properties.⁹ In addition, CNTs have conjugated structure, thermal stability and electrochemical property, which attract widespread attention. Recently, Carbon nanotube is widely used in electrochemical materials, due to its unique structure and excellent performance.¹⁰ Furthermore, metal phthalocyanine compounds as functional organic materials are widely used in different fields such as solar cell, sensor, light-emitting device and nonlinear optical material.^{11,12} Phthalocyanine compounds present certain unique characteristics derived from having two-dimensional conjugated *π*-electronic structure. For instance, phthalocyanines can form complex with different metal elements by accommodating metal elements in the center of the ring; n addition to good chemical stability, Phthalocyanines are both good electron donors and good electron acceptors. Besides, metal phthalocyanines show excellent catalytic chemistry,¹³ photodynamic therapy,¹⁴ electrochemical and photosensitizing properties.^{15–17} Over decades, many research efforts have been focused on the phthalocyanine compounds. Yun Sung Lee and Kee Suk Nahm has studied the influence of phthalocyanine metal complexes to Lithium-Air battery. It is found that the phthalocyanine metal complexes have better battery catalytic activities.¹⁸ Chen et al. have studied the carbonyl-substituted phthalocyanine compounds, they found that materials with high specific capacity for lithium-ion battery.¹⁹ In recent years, our group has studied the influence of different phthalocyanine compounds on Li/SOCl₂ battery, and we found that the phthalocyanine compounds show good catalytic performance to Li/SOCl₂ battery.^{20,21} The main reason is that the delocalized and weakly bound character of π electron clouds in ligand phthalocyanine rings and the d electrons in central transition metal ions can promote electronic gain and loss.²² Thus, phthalocyanines can improve electron transfer as catalysts.

In this paper, metal phthalocyanines modification of carbon nanotubes are synthesized and used as electrocatalysts for the Li/SOCl2 battery. The results show that CNTs and metal phthalocyanines are linked covalently and the modified CNTs possess high electrocatalytic effect on Li/SOCl₂ battery. The modified CNTs cannot only lengthen the discharge time, but also improve the initial voltage of the battery. In addition, the catalysis mechanism of the CNTs-CONH-MPc is speculated and demonstrated by the cyclic voltammetry results.

Experimental

Materials and characterizations.-Carboxylic multi-walled carbon nanotubes was purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. All other reagents were of analytical grade without further purification.

IR spectra were recorded by using a Germany BRUKER VECT022 analyzer with KBr pellets in the infrared region of $400-4000 \text{ cm}^{-1}$.

SEM spectra were tested on a Holland ESEM-FEG, Quanta 400FEG.

XRD patterns were employed by using a Bruker D8 Advance diffractometer equipped with Cu-K α radiation in the 2 θ range of 5–80°.

The XPS spectra were measured on an American PE company HI-540 X-ray photoelectron spectrometer.

The Cyclic Voltammetry was performed on a Chinese Zhengzhou Shiruisi Technology Co. Ltd. RST5000 electrochemical workstation.

Catalyst preparation .- The chemically modified CNTs by metall phthalocyanines (MPc) were prepared as following the method outlined in Scheme 1.

Synthesis of 2,9,16,23-tetranitro-metallophthalocyanine.—The 2,9,16,23-tetranitro-metallophthalocyanines {MTnPc [M = Mn(II),Fe(II), Co(II), Ni(II), Cu(II), Zn(II)]} were synthesized by solvent method. As a route to synthesize FeTnPc, a mixture of 3.00 g 4-nitrophthalimide, 1.20 g FeCl₂ \cdot 4H₂O, 3.00 g urea, 0.10 g (NH₄)₂Mo₂O₇, 1.50 g NH₄Cl was blended and grinded fully in a agate mortar. The grinded mixture was added into a 250 mL threenecked flask with 30 mL jet fuel. The mixture was continually stirred at 185°C for 4 h, and then the dark blue solid was generated.

Purification: When cooling to ambient temperature, the original product was refluxed in 2% HCl solution for 8 h, then the solid was filtered off using G4 funnel under vacuum. The product was refluxed

^zE-mail: jszhao@nwu.edu.cn



(M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Mn(II))

Scheme 1. The synthetic reaction of the MTnPc, MPc and CNTs-CONH-MPc.

in petroleum ether, acetone and dichloromethane for 4 h, respectively. And the precipitate was filtered off using G4 funnel, then the filter cake was washed with 2% NaOH solution until the filtrate became neutral. Finally, the product was refluxed in distilled water and ethyl alcohol, respectively. After filtered, the filter was dried at 100° C for 8 h, then dried under vacuum for 24 h to obtained the powder FeTnPc. Other compounds were synthesized by the same method, only the FeCl₂ · 4H₂O was replaced.

The results of basic information of the compounds listed as follows provide evidence to the structure of the proposed complexes.

FeTnPc - blue green powder, yield 2.51 g (22.37%), and m.p. $>300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 1340, 1524, 1487, 1613, 1134, 1082, 721.

CoTnPc - blueviolet powder, yield 2.70 g (23.98%), and m.p. $>300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 1347, 1510, 1498,1606, 1155, 1097, 736.

NiTnPc - blue violet powder, yield 3.20 g (28.42%), and m.p. $>300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 1353, 1536, 1457, 1619, 1110, 1037, 756.

CuTnPc - azure powder, yield 3.60 g (31.86%), and m.p. > 300°C, IR (KBr pellet, cm⁻¹): 1355, 1532, 1421, 1605, 1155, 1082, 728.

ZnTnPc - blue green powder, yield 2.30 g (20.26%), and m.p. $> 300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 1333, 1517, 1407, 1598, 1104, 1038, 750.

MnTnPc - blue green powder, yield 2.40 g (20.87%), and m.p. $>300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 1340, 1518, 1407, 1605, 1126, 1089, 723.

Synthesis of tetraamino-metallophthalocyanine.—Tetraaminometallophthalocyanines were synthesized by means of the general method. The general synthesis method of tetraaminometallophthalocyanine was as follows: 1.50 g FeTnPc was dissolved in 15mL DMF in a three-necked bottle and heated under stirring. When the mixture was heated to 60°C, 5.8 g sodium sulfide nonahydrate was added to the solution, and refluxed for 24 h. The mixture was poured into 150 mL distilled water after the product cooled to the room temperature. The resulting product was filtered off using G4 funnel. The precipitate was repeatedly washed with 2% HCl solution and 2% NaOH solution, respectively. Then, the product was refluxed again in distilled water and ethyl alcohol for 4 h, respectively. The filtered product was dried at 100°C for 8 h, and dried in vacuum desiccator for 24 h. Finally, the product was obtained. The results of IR spectra of the compounds listed as follows provide evidence to the structure of the proposed complexes.

FePc-atrovirens powder, yield 0.42 g (35.01%), and m.p. > 300° C, IR (KBr pellet, cm⁻¹): 729, 1041, 1123, 1612, 1441, 3346, 3456.

CoPc–atrovirens powder, yield 0.40 g (31.75%), and m.p. > 300°C, IR (KBr pellet, cm⁻¹): 753, 1089, 1141, 1621, 1434, 3329, 3421.

NiPc–atrovirens powder, yield 0.60 g (47.62%), and m.p. >300°C, IR (KBr pellet, cm⁻¹): 744, 1064, 1179, 1631, 1419, 3329, 3419.

CuPc–atrovirens powder, yield 0.39 g (30.95%), and m.p. $> 300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 747, 1078, 1145, 1619, 1427, 3339, 3486.

ZnPc–atrovirens powder, yield 0.37 g (29.37%), and m.p. >300°C, IR (KBr pellet, cm⁻¹): 736, 1037, 1165, 1627, 1436, 3357, 3428.

MnPc-atrovirens powder, yield 0.25 g (19.84%), and m.p. $>300^{\circ}$ C, IR (KBr pellet, cm⁻¹): 718, 1051, 1077, 1624, 1482, 3369, 3487.

Synthesis of CNTs-CONH-MPc.—0.2 g CNTs and 10 mL DMF were added into the 100 mL three-necked bottle with stirring and heated under the N₂ atmosphere. When the temperature reached 76°C, 5 mL SOCl₂ was added dropwise into the solution within 1 h. The mixture was reacted for 24 h at 76°C, and then evaporated the residual SOCl₂. When the temperature reduced to 60°C, 0.4 g MPc was poured to the mixture, and then 1 mL triethylamine was dropped to the solution with a dropping funnel. After 48 h, the mixture was cooled, filtered, refluxed with acetone, dried at 100°C for 8 h, and dried for 24 h in vacuum. Finally, the product of CNTs-CONH-MPc was gained. The result of IR spectra of CNTs-CONH-MPc and basic information provide evidence for the formation.

CNTs-CONH-FePc–dark blue powder, yield 0.43 g (31.75%), IR (KBr pellet, cm⁻¹): 1650, 3426, 1436, 1605, 1112, 1031, 736.

CNTs-CONH-CoPc–dark blue powder, yield 0.38 g (63.33%), IR (KBr pellet, cm⁻¹): 1701, 3431, 1413, 1613, 1134, 1082, 773.

CNTs-CONH-NiPc-dark blue powder, yield 0.73 g (81.11%), IR (KBr pellet, cm⁻¹): 1698, 3393, 1407, 1607, 1163, 1079, 728.

CNTs-CONH-CuPc–dark blue powder, yield 0.32 g (56.14%), IR (KBr pellet, cm⁻¹): 1697, 3341, 1413, 1613, 1155, 1089, 756.

CNTs-CONH-ZnPc-dark blue powder, yield 0.32 g (57.14%), IR (KBr pellet, cm⁻¹): 1716, 3426, 1413, 1610, 1134, 1031, 7158.

CNTs-CONH-MnPc-dark blue powder, yield 0.29 g (76.32%), IR (KBr pellet, cm⁻¹): 1707, 3345, 1473, 1618, 1097, 1031, 713.

Electrochemistry testing.—The whole experiment process was conducted in the glove box with argon gas, in which the relative humidity of atmosphere was less than 2%, and the temperature was kept at 20–23°C. All experimental equipment was kept dry. Carbon film, lithium plate and diaphragm were combined to make experimental battery. 2 mg catalyst (CNTs-CONH-MPc) was added to 2 mL electrolyte, and the mixture was injected into the battery. The discharge test for the assembled battery was evaluated with a constant resistance of 40 Ω until the voltage reached to 2 V. The blank experiment was conducted without any catalyst. In this progress, the relation between the output voltage (U) and the discharge time (t) was measured.

Cyclic voltammetry.—The cyclic voltammetry measurement was conducted on RT5000 electrochemical workstation. The structure diagram of cyclic volammetry was showed in Fig. 1. The test was carried out with three-electrode system: glassy carbon electrode as the working electrode, two lithiums acted as the reference electrode and auxiliary electrode, respectively. Before the tests started, copper wire was handled with sandpaper, glassy carbon electrode was polished with Al_2O_3 powder and then washed with alcohol. The whole experiment process was conducted in the glove box, in which the relative humidity of atmosphere was less than 2%, and the temperature was kept at $20-23^{\circ}C$.

Notes: 1-working electrode, 2-reference electrode, 3-auxiliary electrode, 4-SOCl₂/LiAlCl₄ electrolyte, 5-glass container, 6-lithium plate, 7-copper wire.



Figure 1. The structure diagram of cyclic voltammetry.

Results and Discussion

IR Spectra.—IR spectra of CNTs (a), CNTs-CONH-CuPc (b), CuPc/CNTs (mixed) (c) and CuPc (d) are carried out (Fig. 2). It can be seen from 2a that the absorption peaks of CNTs are not obvious, which is coincide with previous report.²³ As seen from 2d, the double peaks corresponding to amino group are in the region of 3428–3490 cm⁻¹. Combining with the characteristic peaks of phthalocyanine, such as the C=N and C=C stretching vibration peaks at 1400 cm⁻¹ and 1600 cm⁻¹, respectively, the strong peaks of the backbone ring of MPc at 1120 cm⁻¹, 1050 cm⁻¹, 750 cm⁻¹, it confirms that the CuPc is synthesized.²⁴ The new stretches at 1697 cm⁻¹ and 3341 cm⁻¹ in 2b can be assigned to the amido bond stretching vibration, and the FT-IR spectra of 2c do not contain signals associated with the amido bond, which proves the CNTs chemically modified by CuPc.

XRD analysis.—The XRD patterns of CNTs, CNTs-CONH-CuPc, CuPc/CNTs (mixed) and pure CuPc are showed in Fig. 3. The diffraction patterns of pure CNTs exhibits two weak and broad peaks at $2\theta = 25.2^{\circ}$ and 44.6° , which correspond to the (002) and (101) reflections, respectively. As for the pattern of CuPc, six characteristic peaks are at $2\theta = 17.2^{\circ}$, 22.3° , 27.2° , 28.8° , 30.1° and 32.5° , respectively. All diffraction peaks appeares in the low angle range, which conforms to the complex characteristic peak.²⁵ The diffraction patterns of CNTs-CONH-CuPc show both characteristic peaks of CuPc and the CNTs, which further confirms that CuPc bonding with CNTs. For CuPc/CNTs (mixed), five diffraction peaks can be observed at $2\theta = 6.5^{\circ}$, 7.3° , 9.1° , 27.3° , 31.8° . The XRD results manifest that CNTs and CuPc form CNTs-CONH-CuPc.

SEM analysis.—SEM images of CNTs, CNTs-CONH-CuPc, CuPc/CNTs (mixed) and pure CuPc are showed in Fig. 4. SEM



Figure 2. IR spectra of a: CNTs, b: CNTs-CONH-CuPc, c: CuPc/CNTs (mixed), d: CuPc.



Figure 3. X-ray diffraction spectra of a: CNTs, b: CuPc, c: CNTs-CONH-CuPc, d: CuPc/CNTs (mixed).

examination of CNTs reveals that the morphology of CNTs is tubular (Fig. 4a). The morphology analysis on the CNTs-CONH-CuPc shows that the CuPc is linked to the CNTs (Fig. 4b), and no obvious gap between them. Compared Fig. 4c with Fig. 4b, the CuPc particle is suspended in the CNTs surface, not formed bond between CNTs and CuPc. The SEM of CuPc shows irregular bulk morphology (Fig. 4d). SEM study indicates that the CuPc bonds with CNTs and forms target product.



Figure 4. SEM image of a: CNTs, b: CNTs-CONH-CuPc, c: CuPc/CNTs (mixed), d: CuPc.

X-ray photoelectron spectroscopy analysis.—In order to obtain chemical state information of CNTs-CONH-CuPc, XPS analysis has been conducted (Fig. 5). The diffraction signals of carbon, nitrogen, oxygen and copper exist in the whole scanning spectrum, which the diffraction peaks locating at about 290 eV, 400 eV, 532 eV, 940 eV are assigned to the C1s, N1s, O1s, Cu2p, respectively (Fig. 5a). The



Figure 5. a: XPS whole scanning spectra in CNTs-CONH-CuPc, b: core level spectra of Ni2p, c: core level spectra of C1s, d: core level spectra of N1s.



Figure 6. The U-t curves of Li/SOCl₂ battery.

expended Cu2p region reveals two strong peaks with binding energies at 954.6 eV (2p1/2) and 934.8 eV (2p2/3) (Fig. 5b). The analysis of the C1s region manifests one characteristic peak at 285.4 eV, which is corresponding to the C-N bond (Fig. 5c). The N1s energy level signal is located at 398.58 eV, which is attributed to the nitrogen atoms of the C=N in phthalocyanine ring (Fig. 5d). The XPS results further certify that the CNTs are chemical modified by the CuPc through the covalent bond.

Electrocatalytic performance.—Fig. 6 shows the discharge curves of Li/SOCl₂ battery electrocatalyzed by CNTs and CNTs-CONH-MPc (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II)). The blank represents the battery in absence of catalyst, and the initial voltage and the discharge time of blank experiment are 3.13 V and 607 s, respectively. It shows that the battery performances of CNTs-CONH-MPc and CNTs are better than that of blank. The different center metal ions of CNTs-CONH-MPc lead to the different catalytic activities. The results show that the electrocatalytic performance is relate to the metal ions. The reason is that the electrons of the metal ions are shifted into phthalocyanine rings, resulting in acceleration of the catalytic reaction rate. In comparison to the different central metal ions, the discharge time of the battery with CNTs-CONH-CuPc is the longest among the tests (1342 s), and the initial voltage of the battery with CNTs-CONH-CuPc is the maximum among the measurements (3.22 V).

The capacity and the rate capability of the battery are used to evaluate performance of $Li/SOCl_2$ battery electrocatalyzed by catalyst.

The cell capacity of Li/SOCl₂ battery is:

$$C = \int Idt = \int U/Redt = \sum U/Redt = 1/Re \sum U\Delta t$$
[1]

Where I is the discharge current, U stands for the output voltage, Re stands for the electrical resistance, Δt represents the time of discharge. The cell capacity increasing rate of Li/SOCl₂ battery is:

$$X = (C C_0) / C_0 \cdot 100$$
 [2]

Where C and C_0 are the capacity of the Li/SOCl₂ battery and the blank experiment, respectively.

The capacity of the battery electrocatalyzed by CNTs-CONH-CoPc is 95.84 mA \cdot h, which is higher than that of the blank (50.68 mA \cdot h) by the rate of 88.49% (Fig. 7 and Fig. 8).

The electrical testing results are listed in Table I. The maximum initial voltage of Li/SOCl₂ battery catalyzed by CNTs-CONH-CuPc can reach 3.22 V, and the discharge time of CNTs-CONH-CoPc is increased to 1342 s. Compared with blank test, the cell capacities of Li/SOCl₂ battery catalyzed by CNTs-CONH-MPc rise by



Figure 7. The cell capacity of $Li/SOCl_2$ battery CNTs-CONH-MPc (M = Mn, Fe, Co, Ni, Cu, Zn).



Figure 8. The cell capacity increasing rate of $Li/SOCl_2$ battery CNTs-CONH-MPc (M = Mn, Fe, Co, Ni, Cu, Zn).

15.44–88.49%, and the cell capacity of CNTs-CONH-CoPc is extended to $95.84 \text{ mA} \cdot \text{h}$.

All the data indicate that the catalysts can improve the performance of Li/SOCl₂ battery. The main reason is that the carbon nanotube can promote the electronic transmission, and the phthalocyanine has good conjugative effect and enough number of catalytic active sites. When CNTs is bonding with MPc, the synergistic effect between CNTs and MPc can greatly enhance the performance of the Li/SOCl₂ battery.

Table I. The Performance of CNTs-CONH-MPc to Li/SOCl₂.

CNTs-CONH-MPc	initial voltage(V)	discharge time(s)	battery capacity (mA · h)	battery capacity increase rate (%)
Blank	3.09	810	50.68	
CNTs	3.17	773	57.67	13.79
Co(II)	3.20	1342	95.84	88.49
Cu(II)	3.22	919	73.98	34.43
Fe(II)	3.18	1028	73.09	42.39
Mn(II)	3.20	1049	74.23	46.45
Ni(II)	3.19	1196	86.46	69.02
Zn(II)	3.19	817	58.54	15.44

Downloaded on 2017-04-11 to IP 128.138.73.68 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Figure 9. Cyclic voltammogram of the Li/SOCl₂ battery. Scan rate was 100 mV $\rm s^{-1}.$

Cyclic voltammetric analysis.—Cyclic voltammograms are conducted to further investigate the electrocatalytic behavior and the electrocatalytic mechanism. The CVs of bare and CNTs-CONH-MPc in 1.47 mol/L electrolyte are showed in Fig. 9. Two current peaks are observed at 2.6 V and 3.6 V, which are assigned to reductions of SOCl₂ and SCl₂, respectively. That is, two reduction reactions occur in battery system (shown in Eqs. 3 and 4). And The high current peak at 2.6 V, which means that Eq. 3 is the rate-controlling step for the reductive reaction of SOCl₂. Due to no oxidation peak, the reaction of battery is irreversible.

$$SOCl_2 + e \rightarrow 1/2 SCl_2 + 1/2 SO_2 + Cl^-$$
[3]

$$1/2 \operatorname{SCl}_2 + e \to 1/2 \operatorname{S} + \operatorname{Cl}^-$$
^[4]

The shift of the reduction potential and the peak height can testify the electrocatalytic activity of the catalysts. That is, excellent catalyst has bigger reduction potential and higher reduction peak. It can be seen that the order of the peak height is: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} >$ $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+}$, which means that the CNTs-CONH-CoPc has the higher electrocatalytic activity to the Li/SOCl₂ battery. The result is in accordance with results of electrocatalytic performance.^{26–28}

In the metal Phthalocyanines, the ligands and the central metal ions are both the electrocatalytic active sites. By comparing electrocatalytic activity of catalysts with the different central metal ions, it is found that the electrocatalytic activity relates to the electronic configurations of the central metal ions. Among all catalysts, the electrocatalytic performance of Co phthalocyanine is excellent, because the d orbital of Co ion can participate in the electron transition, and the catalytic active sites can achieve an appropriate state through the synergistic effect of the ligands and the central metal ion. Combine with the advantages of CNTs, the CNTs-CONH-CoPc possess the wonderful electrocatalytic performance to Li/SOCl₂ battery.

In order to further verify the electrocatalytic performance of CNTs-CONH-MPc to the Li/SOCl₂ battery, the cyclic voltammetric curves of battery catalyzed by CuPc, CNTs, CNTs-CONH-CuPc and CuPc/CNTs (mixed) are investigated at 100 mV/s (Fig. 10). The reduction peaks potentials and currents of fast reaction step for all samlpes are higher than that of bare, which means that all samples can improve the reaction speed of the fast reaction step. The catalytic activity order is showed as follows: CNTs-CONH-CuPc > CuPc/CNTs(mixed) > CNTs > CuPc > blank. The results show that all the catalysts can improve the electrocatalytic performance to the Li/SOCl₂ battery. Obviously, the modified CNTs-CONH-CuPc is superior to others. The main reason is that there are synergistic effect between the phthalocyanine and the CNTs. CNTs can enhance the surface area and accelerate the electron transfer, and the phthalocya-



Figure 10. Comparative cyclic voltammetries of a: blank, b: CuPc, c: CNTs-CONH-CuPc, d: CNTs e: CuPc/CNTs (mixed).

nine has good conjugative effect and abundant catalytic active sites. So, the electrocatalytic performances of the CNTs bonding with MPc performs best among them.

In order to investigate the function between the phthalocyanine and the CNTs, the cyclic voltammetric curves are also recorded by different scan rates. Fig. 11 shows CV curves at different scanning rates (40 ~ 100 mV/s) in LiAlCl₄/SOCl₂ solution containing CNTs-CONH-CuPc. It can be seen that the reduction peaks are enhanced with the raise of the scanning rate. A linear equation is obtained by fitting the data (log i_{pc} vs log v (i_{pc} : current of the rate-controlling step, v: scan rate)) (Fig. 12). The obtained linear equation is y = 36.654x – 101.97, with the correlation coefficient of 0.9845, which indicates the function of electrode surface is mainly diffusion control.

Catalytic mechanism.—Other group has studied the catalytic mechanism of the Li/SOCl₂ battery catalyzed by metallophthalocyanines.^{29,30} On the basis of the previous study and CV the result, the process of the reduction of SOCl₂ catalyzed by CNTs-CONH-MPc may undergo three steps (Fig. 13):

$$CNTs-CONH-MPc + SOCl_2 \rightarrow CNTs-CONH-MPc \cdot SOCl_2$$
 [5]

$$CNTs-CONH-MPc \cdot SOCl_2 + e^{-}$$

$$\rightarrow CNTs-CONH-MPc \cdot SOCl + Cl^{-} \qquad [6]$$



Figure 11. Representative cyclic voltammograms for CNTs-CONH-CuPc at different scan rates.



Figure 12. Plot of scan rate versus root of the sweep rate for CNTs-CONH-CuPc.

$CNTs-CONH-MPc \cdot SOCl + e^{-1}$

$$\rightarrow 1/2 \text{ S} + 1/2 \text{ SO}_2 + \text{Cl}^- + \text{CNTs-CONH-MPc}$$
 [7]

The first step is that the SOCl₂ bonds with catalyst to form an adduct CNTs-CONH-MPc · SOCl₂. In the second step, the adduct gains one electron and decomposes into MPc-CNTs · SOCl and Cl⁻. In the finally step, CNTs-CONH-MPc · SOCl gain another electron by the fast electron transfer reaction, accompanying with the return of the catalyst and forming S, SO₂ and Cl⁻. CNTs is a good conductor of electronic, and metal phthalocyanines possess good electrochemical properties. The CNTs-CONH-MPc has beneficial effects on electron shift in the electrocatalysts, due to their excellent electrochemical properties and the synergistic effect of CNTs and metal phthalocyanines. The For these reasons, the CNTs-CONH-MPc possess excellent catalytic activity.

Conclusions

In this paper, chemically modified CNTs were synthesized by bonding with metal phthalocyanines, and the electrical performance of Li/SOCl₂ battery catalysed by CNTs-CONH-MPc were studied. The results manifested that metal phthalocyanines are bonding with CNTs by chemical bond, and the obtained CNTs-CONH-MPc catalyst shows excellent catalytic activity. The experiment results show that all catalysts can enhance the electrical performance to Li/SOCl₂ battery, especially, the cell capacity of Li/SOCl₂ battery catalyzed by CNTs-CONH-CoPc can extended to 95.84 mA \cdot h, with increase by 88.49%. Besides, it is found that the synergistic effect between the CNTs and



Figure 13. The catalytic mechanism of the CNTs-CONH-MPc to Li/SOCl₂ battery.

the phthalocyanine is the main reason for improve the performance of $Li/SOCl_2$ battery.

Acknowledgments

The authors thank the National Natural Science Foundation of China (Nos. 21371143, 21671157 and 21501139) for the financial support of this work.

References

- George Ting-Kuo Fey, Ming-Chih Hsieh, and Yu-Chi Chang, "Mass transport and kinetic aspects of thionyl chloride reduction at the platinum microelectrode," *Journal* of power sources, 97, 606 (2001).
- Bei Xu et al., "Investigation of binuclear metal phthalocyanines as electrocatalysts for Li/SOCl2 battery," *Journal of Solid State Electrochemistry*, 17, 2391 (2013).
- P. A. Bernstein and A. B. P. Lever, "Two-electron oxidation of cobalt phthalocyanines by thionyl chloride. Implications for lithium/thionyl chloride batteries," *Inorganic chemistry*, 29, 608 (1990).
- H. Zhao, S. Wang, H. Cheng, and K. Dong, & W Liu, "Electrochemical performance of LiAlCl4/SOC12 electrolyte with 2, 2'-bipyridine in Li/SOC12 batteries," *Int. J. Electrochem. Sci*, 8, 9752 (2013).
- Woo-Seong Kim and Yong-Kook Choi, "Electrocatalytic effects of thionyl chloride reduction by polymeric Schiff base transition metal (II) complexes," *Applied Catalysis A: General*, 252, 163 (2003).
- Young-ok Ko and Chul-Tae Lee, "Effects of the structural characteristics of carbon cathode on the initial voltage delay in Li/SOCl 2 battery," *Journal of Industrial and Engineering Chemistry*, 18, 726 (2012).
- Zhanwei Xu et al. "Influence of the electronic configuration of the central metal ions on catalytic activity of metal phthalocyanines to Li/SOCI 2 battery," *Journal of power sources*, **194**, 1081 (2009).
- Zhanwei Xu et al. "Effect of N atoms in the backbone of metal phthalocyanine derivatives on their catalytic activity to lithium battery," *Journal of Molecular Catalysis A: Chemical*, **318**, 101 (2010).
- 9. S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, **354**, 56 (1991).
- Mihaela Baibarac et al., "Electrochemically functionalized carbon nanotubes and their application to rechargeable lithium batteries," *Small*, 2, 1075 (2006).
- Baiqing Zhu et al., "Novel planar binuclear zinc phthalocyanine sensitizer for dyesensitized solar cells: Synthesis and spectral, electrochemical, and photovoltaic properties," *Journal of Molecular Structure*, **1079**, 61 (2015).
- Ling Liu et al., "Electrochemical sensors based on binuclear cobalt phthalocyanine/surfactant/ordered mesoporous carbon composite electrode," *Analytica chimica acta*, 673, 88 (2010).
- Y. Jiang, Y. Lu, X. Lv, D. Han, Q. Zhang, L. Niu, and W. Chen, "Enhanced catalytic performance of Pt-free iron phthalocyanine by graphene support for efficient oxygen reduction reaction," ACS Catalysis, 3(6), 1263 (2013).
- Haifeng Liang et al., "Photoconductivity of reduced graphene oxide and graphene oxide composite films," *Thin Solid Films*, **521**, 163 (2012).

- M. A. Özdag, T. Ceyhan, and H. G. Yaglioglu, "Optical limiting properties of trimeric metallo-phthalocyanines/polymer composite films," *Optics & Laser Technology*, 43, 992 (2011).
- Yu Wang et al., "Two-dimensional iron-phthalocyanine (Fe-Pc) monolayer as a promising single-atom-catalyst for oxygen reduction reaction: a computational study," *Nanoscale*, 7, 11633 (2015).
- Y. H. Bian, J. S. Chen, S. T. Xu, Y. L. Zhou, L. J. Zhu, and Y. Z. Xiang, "The effect of a hydrogen bond on the supramolecular self-aggregation mode and the extent of metal-free benzoxazole-substituted phthalocyanines," *New Journal of Chemistry*, 39, 5750 (2015).
- A. Arul, M. Christy, Y. Oh M., S. Lee Y., and S. Nahm K., "Nanofiber Carbon-Supported Phthalocyanine Metal Complexes as Solid Electrocatalysts for Lithium-Air Batteries," *Electrochimica Acta*, 218, 335 (2016).
- J. Chen, Q. Zhang, M. Zeng, N. Ding, Z. Li, and S. Zhong, "Carboxyl-conjugated phthalocyanines used as novel electrode materials with high specific capacity for lithium-ion batteries," *Journal of Solid State Electrochemistry*, 20, 1285 (2016).
- Zhijiao Liu et al., "Graphene/phthalocyanine composites and binuclear metal phthalocyanines with excellent electrocatalytic performance to Li/SOCI 2 battery," *Electrochimica Acta*, 187 (2016): 81.
- Li Xiang, HUANG Xinyue, GAO Ruimin, ZHANG Ronglan, and ZHAO Jianshe, "Improved performance of Li/SOCI 2 batteries using binuclear metal azaphthalocyanines as electrocatalysts," *Electrochimica Acta* (2016).
- R. Zhang, J. Wang, B. Xu, X. Huang, Z. Xu, and J. Zhao, "Catalytic activity of binuclear transition metal phthalocyanines in electrolyte operation of lithium/thionyl chloride battery," *Journal of The Electrochemical Society*, **159**, H704 (2012).
 M. Zu, Q. Li, Y. Zhu et al., "The effective interfacial shear strength of carbon nanotube
- M. Zu, Q. Li, Y. Zhu et al., "The effective interfacial shear strength of carbon nanotube fibers in an epoxy matrix characterized by a microdroplet test," *Carbon*, **50**, 1271 (2012).
- Z. Pu, K. Jia, and X. Liu, "Covalent grafting of a-CNTs on copper phthalocyanine for the preparation of PEN nanocomposites with high dielectric constant and high thermal stability," *Journal of Materials Science: Materials in Electronics*, 26, 8922 (2015).
- K. S. Rajmohan and R. Chetty, "Enhanced nitrate reduction with copper phthalocyanine-coated carbon nanotubes in a solid polymer electrolyte reactor," *Journal of Applied Electrochemistry*, 47, 63 (2017).
- W. S. Kim, Y. K. Choi, and K. H. Chjo, "Studies on electrochemical properties of lithium/oxyhalide cell: Electrocatalytic effects on the reduction of thionyl chloride," *Bulletin of the Korean Chemical Society*, 15, 456 (1994).
- Y. K. Choi, B. S. Kim, and S. M. Park, "Electrochemical reduction of thionyl chloride studied by cyclic voltammetry, chronocoulometry, and chronoamperometry," *Journal* of *The Electrochemical Society*, **140**, 11 (1993).
- W. S. Kim, W. J. Sim, K. Chung et al., "Studies on electrochemical properties of thionyl chloride reduction by Schiff base metal (II) complexes," *Journal of power sources*, **112**, 76 (2002).
- Seung-Bok Lee, Su-II Pyun, and Eung-Jo Lee, "Effect of the compactness of the lithium chloride layer formed on the carbon cathode on the electrochemical reduction of SOCI 2 electrolyte in Li–SOCI 2 batteries," *Electrochimica Acta*, 47, 855 (2001).
- Woo-Seong Kim and Yong-Kook Choi, "Electrocatalytic effects of thionyl chloride reduction by polymeric Schiff base transition metal (II) complexes," *Applied Catalysis A: General*, 252, 163 (2003).