Journal of Electroanalytical Chemistry 808 (2018) 8–13

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

A series of new Phthalocyanine derivatives with large conjugated system as catalysts for the Li/$SOCl_2$ battery

Yan Gao[a], Liangting Chen[a], Mengkai Quan[a], Gai Zhang[b], Ying Zheng[c], Jianshe Zhao[a,*]

[a] Key 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, China
[b] School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710021, China
[c] Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

ARTICLE INFO

Keywords:
Metallophthalocyanine
Li/$SOCl_2$ battery
Conjugated system
Catalyst

ABSTRACT

In order to overcome the disadvantages of Li/$SOCl_2$ battery, such as low voltage and small capacity, a series of phthalocyanine derivatives (MPcOc) as catalysts were added into the electrolyte. In this work, new phthalocyanines were synthesized by the microwave method, and this technique greatly shortened the reaction time. The catalysts were characterized by techniques including the FT-IR, UV–vis, ICP, SEM and XRD. The electrocatalytic performances of the MPcOc to Li/$SOCl_2$ battery were evaluated by electrochemical testing. The synthesized catalysts showed excellent performance with the capacities increasing by 19.34–55.64%. Based on cyclic voltammetry measurements, the function of electrode surface and reaction mechanism were proposed.

1. Introduction

In recent years, lithium/thionyl chloride (Li/$SOCl_2$) battery as a new type of energy resource causes wide attention [1]. Li/$SOCl_2$ battery, a kind of typical non-aqueous electrolyte battery, is extensively applied in the industrial and military areas [2–4]. Compared with other batteries, the Li/$SOCl_2$ battery possesses a lot of advantages such as high specific power, high voltage, high specific energy, and low temperature performance [5–8]. Li/$SOCl_2$ battery is a primary battery. The character evaluation indexes of Li/$SOCl_2$ battery generally consist of battery capacity, voltage, internal resistance, battery ratio and so on. In practical application, battery capacity is the most important indicator. The Li/$SOCl_2$ battery is composed of anode, cathode and non-aqueous electrolyte: the lithium is employed as the cathode, carbon as the anode, and the mixed solution ($SOCl_2$/$LiAlCl_4$) as the electrolyte [9]. When the battery is discharging, lithium loses an electron to become lithium ion, and $SOCl_2$ is reduced. The final products are LiCl, SO_2 and S (Eqs. 1–3) [10]. The open-circuit voltage of Li/$SOCl_2$ battery is 3.65 V, but the actual voltage value is less than the theoretical value. The passivation layer of LiCl forming on the anode surface prevents the electronic transmission and reduces the virtual voltage [11–12]. In order to overcome the the disadvantages of battery in practical application, many workers have done a lot of research. At present, the research on how to improve performance mainly includes two aspects: one is select the battery anode material, the other is improve the electrolyte. Xiao-Dong Zhu et al. reported that acetylene black/graphene hybrid as a cathode material has positive effects on discharging performance of Li/$SOCl_2$ battery [13]. Jun Li et al. used metalloporphyrins as the catalyst for improve battery performance; they found that materials have potential application in Li/$SOCl_2$ battery [14].

$$\text{Anode: } Li - e \rightarrow Li^{+} \quad (1)$$

$$\text{Cathode: } 2SOCl_2 + 4e^{-} \rightarrow S\downarrow + SO_2\uparrow + 4Cl^{-} \quad (2)$$

$$\text{Cell: } 2SOCl_2 + 4Li \rightarrow S\downarrow + SO_2\uparrow + 4LiCl\downarrow \quad (3)$$

Phthalocyanines are first found by Braun and Tcheriac in 1907, which contain macrocyclic aromatic conjugation system [15]. Synthetic Phthalocyanines with special structure own excellent stability, unique chemical property, low cost and low toxicity, which make it have high application potential [16–19]. Now, Phthalocyanines as catalysts are widely used in catalysis chemistry, oxidative desulfurization, photochemistry and battery catalysis [20–23]. So far, the ways of synthesizing phthalocyanines mainly include liquid phase method and solid phase method [24–26]. There are some drawbacks in traditional solution method, such as long reaction time, high toxicity and high cost [27]. Solid phase method is a method to prepare the target product by directly heating the reactant, and traditional solid phase method requires reactant to react for several hours at a higher temperature. Therefore, low efficiency and high costs exist in traditional solid phase method. Microwave method, as a new green method, have many

* Corresponding author.
E-mail address: jszhao@nwu.edu.cn (J. Zhao).

https://doi.org/10.1016/j.jelechem.2017.11.062
Received 29 June 2017; Received in revised form 22 November 2017; Accepted 23 November 2017
Available online 23 November 2017

advatages, such as short reaction time, low toxicity, low cost. Therefore, microwave method is used in our paper to reduce reaction time and increase reaction efficiency. Recently, our group has researched the impact of phthalocyanines and their derivatives to Li/$SOCl_2$ battery [28,29]. We find that the phthalocyanine compounds show good catalytic performance to Li/$SOCl_2$ battery. The statistical data show that the catalytic activity to Li/$SOCl_2$ battery affected by the central metals [30]. And the effect of substituent group has different influence on catalytic performance [31]. Besides, the conjugation structure is also the main influencing factor.

In this paper, a series of metalphthalocyanines, with macrocyclic aromatic conjugation system, are designed, synthesized and characterized. The complexes have been characterized by elemental analysis, IR, UV–vis and XRD at room temperature. The electrical testing results indicate that all compounds possess excellent performance on Li/$SOCl_2$ battery. Moreover, the reaction mechanism of the catalysts is proposed and verified by the cyclic voltammetry.

2. Experimental procedure

2.1. Materials and method

Perylene-3,4,9,10-tetracarboxylic dianhydride was obtained from J&K China Chemical Ltd., 4-Nitrophthalimide was purchased from TCI (shanghai) Development Co., Ltd. And all other reagents are analytical grades without further purification.

$LiAlCl_4$/$SOCl_2$ electrolyte (battery grade), lithium foil (battery grade) and C film (battery grade) were purchased from Xi'an Institute of Electrical and Mechanical Services Information.

Elemental analysis (C, H and N) was performed on a Germany Vario EL III CHNOS analyzer. IR spectra were measured on a Germany BRUKER VECT022 analyzer by using KBr pellets in the infrared region of 400–4000 cm^{-1}. Absorption spectra were recorded on a PE-40P UV spectrometer in the range of 300–700 nm. The cyclic voltammetry was performed on a Chinese Zhengzhou Shiruisi Technology Co. Ltd., RST5000 electrochemical workstation.

2.2. Preparation of octocarboxyphthalocyanine

The catalysts were prepared by microwave method (scheme 1). As a route to synthesize MPcOc, perylene-3,4,9,10-tetracarboxylic dianhydride (0.30 g), urea (5.00 g), $(NH_4)_2Mo_2O_7$ (1.15 g), NH_4Cl (1.10 g), M$(OAc)_2{\cdot}nH_2O$ (1.8×10^{-4} mol) were mixed and grinded evenly with agate mortar. Then the mixture transferred into a 100 mL crucible. The mixture was exposed to microwave radiation with 400 W output power for 3 min and 640 W for 5 min. After cooling to room temperature, original product was obtained. The octocarboxyphthalocyanines with different central metal were performed with same method in presence of various metal salts.

Purification: the solid product was poured into a 250 mL three-necked bottle and refluxed for 24 h in HCl solution (2%). Then the reacted mixture was filtered off by using G4 funnel under vacuum and dried for 12 h at 100 °C. The solid product was refluxed again for 8 h in deionized water, methyl alcohol, acetone, chloroform, absolute ethanol, respectively. After filtering through G4 funnel, the obtained material was dried for 12 h at 100 °C in the vacuum desiccator. The goal product was obtained.

The basic information and elements analyses providing the evidence for their structure were presented as follows:

MnPcOc: dark purple powder, yield 0.2937 g (92.01%), and m.p. > 300 °C, Anal. Calcd. for $C_{96}H_{42}N_8O_{16}Mn$ - C 71.25, H 2.62, N 6.92; Found (%) - C 71.21, H 2.58, N 6.88.

FePcOc: violet powder, yield 0.2831 g (88.58%), and m.p. > 300 °C, Anal. Calcd. for $C_{96}H_{42}N_8O_{16}Fe$ - C 71.21, H 2.61, N 6.92; Found (%) - C 71.29, H 2.89, N 6.91.

CoPcOc: dark purple powder, yield 0.2820 g (87.90%), and m.p. > 300 °C, Anal. Calcd. for $C_{96}H_{42}N_8O_{16}Co$ - C 71.07, H 2.61, N 6.91; Found (%) - C 71.09, H 2.72, N 6.79.

NiPcOc: aubergine powder, yield 0.2872 g (89.55%), and m.p. > 300 °C, Anal. Calcd. for $C_{96}H_{42}N_8O_{16}Ni$ - C 71.08, H 2.61, N 6.91; Found (%) - C 71.15, H 2.68, N 6.97.

CuPcOc: dark purple powder, yield 0.2610 g (80.93%), and m.p. > 300 °C, Anal. Calcd. for $C_{96}H_{42}N_8O_{16}Cu$ - C 70.87, H 2.60, N 6.89; Found (%) - C 70.79, H 2.53, N 6.81.

ZnPcOc: dark purple powder, yield 0.2760 g (87.90%), and m.p. > 300 °C, Anal. Calcd. for $C_{96}H_{42}N_8O_{16}Zn$ - C 70.79, H 2.60, N 6.88; Found (%) - 70.71, H 2.44, N 6.65.

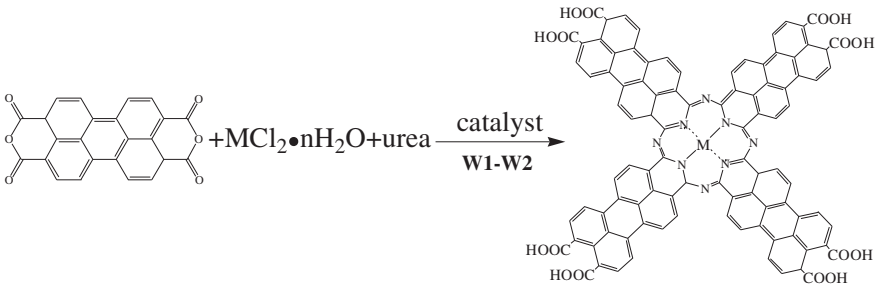
2.3. Electrochemistry testing

In this paper, the structure of test circuit was showed in Fig. 1a. The whole testing system includes simulated cell, load resistance and electrochemical workstation. The structure of simulated cell was showed in Fig. 1b. Simulated battery was made up of three electrodes system: cathode, anode and electrolyte. The cathode preparations: the cathode material was obtained by mixing acetylene black and conductive agent in diluted Teflon emulsion, mass ratio of black and conductive agent 9:1. The mixture was stirred until forming cream. Then, the cream was repeated rolling into a certain thick film via using a heated roller machine. The film was dried at 150 °C for 12 h and shaped into a certain size according to the cathode.

Battery assemblies: the whole experimentation was carried out in the glove box with dry air, in which the relative humidity was < 2%, and the temperature was maintained at 20–28 °C. In the meantime, all experimental apparatus were kept dry. The electrochemical catalysts (MPcOc) (2 mg) were added into the electrolyte (2 mL). The performance of the battery was carried out with a constant resistance of 40 Ω and an average current density of 70 mA cm^{-2} until the battery continuously discharged to 2 V. In the progress, relations between the output voltage (U) and the discharge time (t) were measured.

2.4. Cyclic voltammetry

The CV measurement was tested on RST5000 electrochemical workstation by using three-electrode system, setting the scanning range between 0 and 5 V. The three-electrode system is consisted of the reference electrode, glassy carbon electrode and auxiliary electrode. The current voltage curves were recorded on electrochemical workstation.



Scheme 1. The synthetic route of MPcOc.