Short communication

Influence of the electronic configuration of the central metal ions on catalytic activity of metal phthalocyanines to Li/SOCl$_2$ battery

Zhanwei Xu [a,b], Jianshe Zhao [b], Hejun Li [a,*], Kezhi Li [a], Zeyuan Cao [a], Jinhua Lu [a]

[a] C/C Composites Research Center, National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an 710072, PR China
[b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry, Northwest University, Xi'an 710069, PR China

ARTICLE INFO

ABSTRACT

The relative energy of Li/SOCl$_2$ battery whose electrolyte contains the transition metal phthalocyanines is used to evaluate the catalytic activity of the compounds. The energy of Li/SOCl$_2$ battery whose electrolyte contains transition metal phthalocyanines-tetracarboxylic acid (MPcTc) and metal phthalocyanines-tetrasulfonic acid (MPcTs) (M = Mn^{2+}, Ni^{2+}) increases by approximately 62–106%, the energy of Li/SOCl$_2$ battery whose electrolyte contains MPcTc and MPcTs (M = Fe^{2+}, Co^{2+}) increases by approximately 32–52%, and the energy of Li/SOCl$_2$ battery whose electrolyte contains CuPcTc and CuPcTs is similar to that of the cell in the absence of these complexes. It shows that the electronic configuration of the central metal ion strongly influences the catalytic activity of metal phthalocyanine to Li/SOCl$_2$ battery. To the same ligand, the compound whose central metal ion with electronic configuration d^9 is inactive; the compound whose central metal ion with electronic configuration d^4 or d^8 exhibits relatively high catalytic activity; and the compound whose central metal ion with electronic configuration d^5 or d^7 exhibits relatively low catalytic activity. Three possible routes of catalytic reduction of SOCl$_2$ by transition metal phthalocyanine compound are proposed to interpret the results.

1. Introduction

The lithium-thionyl chloride (Li/SOCl$_2$) battery is one practical battery with high discharge voltage and energy density. The excellent electrochemical performance of Li/SOCl$_2$ primary batteries and reserve batteries has aroused great interest over the past two decades [1–6]. However, the energy of Li/SOCl$_2$ battery in practice is much lower than that in theory, which renders a great challenge in the application of Li/SOCl$_2$ battery. Metal phthalocyanine is one interesting compound which has a conjugated macromolecule, exhibiting an outstanding performance in photovoltaic cell, sensor and catalysis industry [7–9]. Many works on metal phthalocyanines as the cathode catalyst to Li/SOCl$_2$ battery have been reported [10,11].

The mechanism of the catalytic reduction of SOCl$_2$ by metal phthalocyanine compounds has been demonstrated in many previous works [12–15]. It is required that the compound as the catalyst of the battery must be readily oxidizable/reducible [1]. However, few works discussed or analyzed the factors that affect the catalytic activity of the metal phthalocyanine compounds in depth. In fact, the electronic configuration of central metal ion of the metal phthalocyanines has a great influence on electronic accep-

tor/donor property of the metal phthalocyanine compound and probably affects the catalytic activity of the compound further. In this paper we focus on the analysis of the potential effect of the electronic configuration of the central metal ion on the catalytic activity of the metal phthalocyanine compound.

2. Experimental

The relative energy of Li/SOCl$_2$ battery was used to evaluate the catalytic activity of the complexes. Metal phthalocyanines-tetracarboxylic acid (MPcTc) and metal phthalocyanines-tetrasulfonic acid (MPcTs) (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) were synthesized to add into the solution of LiAlCl$_4$/SOCl$_2$ electrolyte.

2.1. Preparation of the MPcTc and MPcTs

MPcTc and MPcTs (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) were synthesized by microwave reaction, and were characterized by element analysis and IR (shown in supplementary material).

2.2. Electrochemistry

The electrochemical measurements of Li/SOCl$_2$ battery whose electrolyte contains 5×10^{-3} mol L^{-1} MPcTc (MPcTs) complexes (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, respectively) were carried out by the specially designed test cells. The discharge of the Li/SOCl$_2$
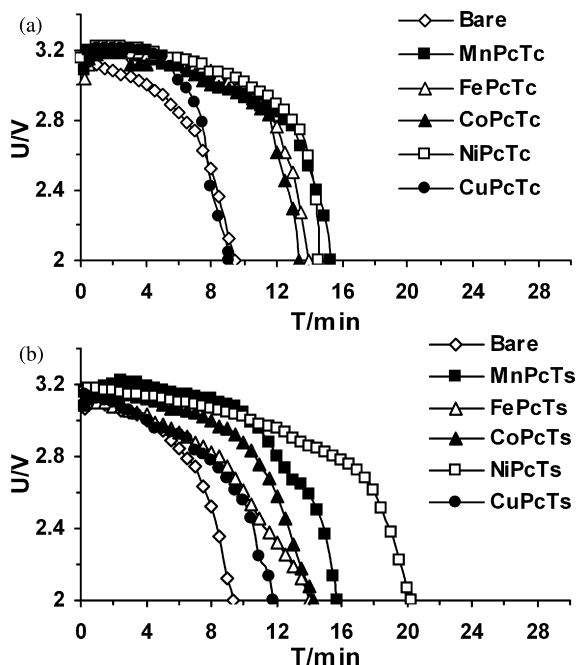
Fig. 1. The discharge curves of lithium-thionyl chloride battery (LiAlCl₄–SOCl₂ electrolyte, 1.47 M; constant discharge resistance, 40 Ω; apparent electrode area, 1 cm²). (a) Electrolyte solution containing MPcTc (M = Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺, respectively), 5×10^{-3} M. (b) Electrolyte solution containing MPcTs, 5×10^{-3} M.

Fig. 2. The compounds and the relative capacity of Li/SOCl₂ battery catalyzed.

battery was operated at a constant resistance 40 Ω, and was stopped when the voltage reached 2 V. $1.47 \, \text{mol L}^{-1}$ LiAlCl₄–SOCl₂ electrolyte solution was used. All experiments were implemented in a glove box under an argon atmosphere (MBRAUN, MB-BL-01).

3. Results and discussion

The discharge curves of Li/SOCl₂ battery are shown in Fig. 1. The relative energy (X) of Li/SOCl₂ battery is used to evaluate the electrochemical effects of Li/SOCl₂ battery catalyzed by the compounds.

The energy of Li/SOCl₂ battery is

$$C = \int P \, dt = 1/\text{Re} \sum U^2 \, \Delta t \tag{1}$$

where P is the discharge power of the battery, Re is the constant resistance, U is the voltage discharged in the test.

The relative energy of the battery is

$$X(\%) = \frac{C}{C_0} \times 100 \tag{2}$$

where C stands for the energy of the battery, C_0 stands for the energy of the battery in the absence of complexes.

The energy of Li/SOCl₂ battery whose electrolyte contains MPcTc and MPcTs (M = Mn²⁺, Ni²⁺) is approximately 62–106% higher than that of the cell in the absence of complexes, whereas the energy of Li/SOCl₂ battery whose electrolyte contains MPcTc and MPcTs (M = Fe²⁺, Co²⁺) both of which have relatively low catalytic activity, is approximately 32–52% higher than that of the cell in the absence of complexes. By contrast with the two kinds of compounds above, CuPcTc and CuPcTs are inactive, and the energy of Li/SOCl₂ battery whose electrolyte contains them are similar to that of the cell in the absence of complexes (shown in Fig. 2a and b). The results indicate that the electronic configuration of central metal ions (M²⁺) is the key factor affecting the catalytic activity of the compounds to Li/SOCl₂ battery. To the same ligand, the compound whose central metal ion with electronic configuration d⁴ or d⁸, such as Mn²⁺ and Ni²⁺, exhibits relatively high catalytic activity; the compound
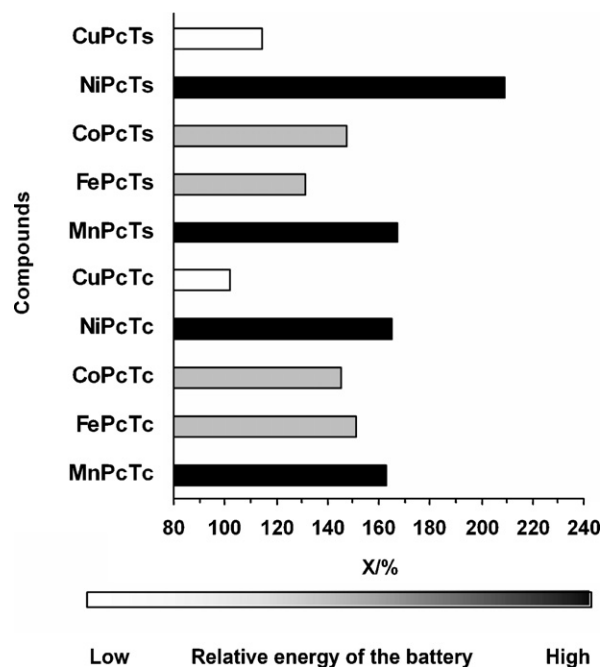
whose central metal ion with electronic configuration d⁵ or d⁷, such as Fe²⁺ and Co²⁺ has relatively low catalytic activity; and the compound whose central metal ion with electronic configuration d⁹, such as Cu²⁺, is inactive.

The mechanism of the reduction of SOCl₂ by MPc has been demonstrated by Doddapaneni and Bernstein [12,13]. Doddapaneni has shown there exist three sites Co⁺, Co²⁺, and Co³⁺ in the process of the reduction of SOCl₂ by CoPc. Bernstein has shown the formation of the adduct CoPc·SOCl₂ is the key step in this catalytic reduction reaction.

On the basis of the results and the mechanism of the catalytic reduction by metal phthalocyanine demonstrated by Doddapaneni and Bernstein, three possible routes are proposed to show the process of the reduction of SOCl₂ catalyzed by M²⁺L (L = PcTc, PcTs) (shown in Fig. 3).

(1) SOCl₂ is adsorbed by M²⁺L, the O atom of SOCl₂ coordinates to M²⁺ of M²⁺L, an adduct M²⁺L·SOCl₂ is formed.

$$M^{2+}L + SOCl_2 \rightarrow M^{2+}L \cdot SOCl_2 \tag{3}$$
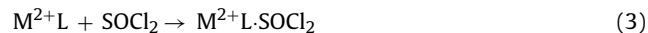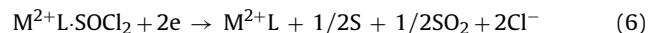
(2) After that, there are three possible routes that M²⁺L·SOCl₂ succeeds catalyzing the reduction of SOCl₂.

Route 1 is that one electron is accepted by M²⁺L·SOCl₂, M²⁺L·SOCl₂ is reduced, and turns into [M³⁺L]⁺, S, SO₂ and Cl⁻. [M³⁺L]⁺ accepts one electron, and turns into M²⁺L.

$$M^{2+}L \cdot SOCl_2 + e \rightarrow [M^{3+}L]^+ + 1/2S + 1/2SO_2 + 2Cl^- \tag{4}$$

$$[M^{3+}L]^+ + e \rightarrow M^{2+}L \tag{5}$$
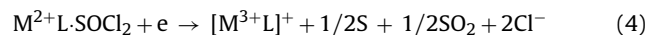
Route 2 is that two electrons are accepted by the ligand L, M²⁺L·SOCl₂ is reduced, and turns into M²⁺L, S, SO₂ and Cl⁻.

$$M^{2+}L \cdot SOCl_2 + 2e \rightarrow M^{2+}L + 1/2S + 1/2SO_2 + 2Cl^- \tag{6}$$

(3) Route 3 is that three electrons are accepted by M²⁺L·SOCl₂, M²⁺L·SOCl₂ is reduced, and turns into [M⁺L]⁻, S, SO₂ and Cl⁻. A dismutation reaction occurs between [M⁺L]⁻ and [M³⁺L]⁺.

$$M^{2+}L \cdot SOCl_2 + 3e \rightarrow [M^+L]^- + 1/2S + 1/2SO_2 + 2Cl^- \tag{7}$$
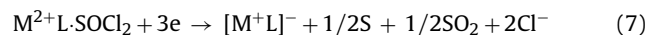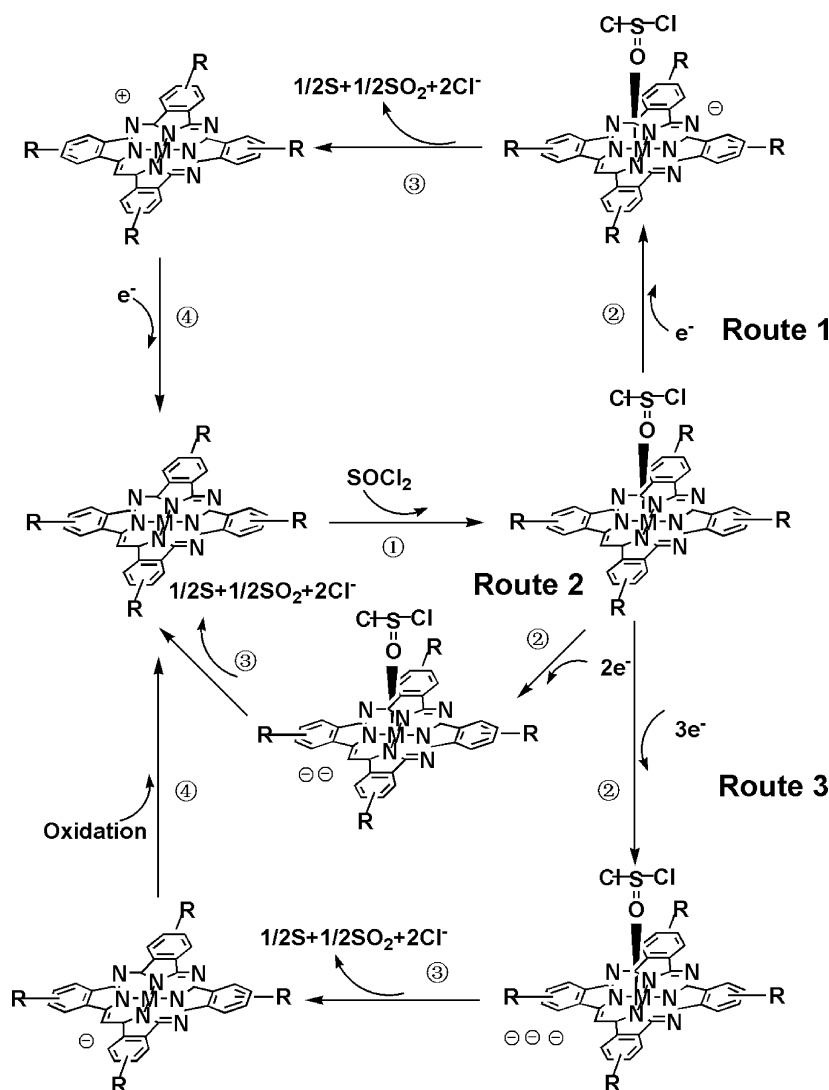
Fig. 3. The three possible routes of the process of the reduction of SOCl$_2$ catalyzed by ML.

$$[M^{3+}L]^+ + [M^+L]^- \rightarrow 2\,M^{2+}L \tag{8}$$

The overall catalytic activity of the compounds to lithium battery depends on both the competitive and cooperative process of the three routes. To the same ligand, the three routes are primarily controlled by the electronic configuration of the central metal ions of the compounds. We can rely on the Jahn–Teller effect existing in transition metal complexes such as the Mn^{3+} and Cu^{2+} complexes to explain the mechanism [16,17]. To form octahedral complexes is by far the most common trend which occurs in the second-raw transition metal ions. However, due to the Jahn–Tellar effect, the central metal ions with the electronic configuration d^4, d^9, are liable to form square planar complexes. To Mn^{2+}L, whose d electronic configuration is 3d^5 and is liable to form octahedral complex, the adduct M^{2+}L·SOCl$_2$ forms and catalyzes the reduction of SOCl$_2$ through the three routes. Among the three routes, the route 1 plays a predominant role because the electronic configuration of Mn^{3+} is 3d^4, and have the great trend to form square planar complex and to enhance the process of the formation of [Mn^{3+}L]$^+$, S, SO$_2$ and Cl$^-$ during the reduction of Mn^{2+}L·SOCl$_2$, therefore enhancing the catalytic reaction. As to Ni^{2+}L, whose configuration of d electron is 3d^8 and is liable to octahedron coordinate. Among the three routes that the adduct Ni^{2+}L·SOCl$_2$ forms, route 3 plays a predominant role due to that the electron configuration of Ni$^+$ is 3d^9, and have the great

trend to form square planar complex, so it will enhance the process of the formation of [Ni$^+$L]$^-$, S, SO$_2$ and Cl$^-$ during the reduction of Ni^{2+}L·SOCl$_2$, therefore enhancing the catalytic reaction. Therefore Mn^{2+}L and Ni^{2+}L exhibit excellent catalytic activity to Li/SOCl$_2$ battery. But to Cu^{2+}L, whose d electronic configuration is 3d^9 and have the great trend to form square planar complex rather than octahedral complex, the O atom of SOCl$_2$ cannot coordinate to Cu^{2+}, Cu^{2+}L is inactive as a result. By contrast with all the complexes above, the d electronic configurations of Fe^{2+} and Co^{2+} are 3d^6 and 3d^7, respectively and are liable to form octahedral complexes. The O atom of SOCl$_2$ coordinates to Fe^{2+} and Co^{2+} easily, after that, the adduct Fe^{2+}L·SOCl$_2$ (Co^{2+}L·SOCl$_2$) forms and the electron was accepted/donated through the three routes. Comparing to M^{2+} and Ni^{2+}, there is no fast catalytic route in the process of the reduction of SOCl$_2$ catalyzed by Fe^{2+}L and Co^{2+}L, so Fe^{2+}L and Co^{2+}L exhibit relatively low catalytic activity to lithium battery.

4. Conclusions

The influence of the electronic configuration of the central metal ion on catalytic activity of metal phthalocyanines to Li/SOCl$_2$ battery has been shown in this paper. The metal phthalocyanines whose central metal ion of electronic configuration d^9 are inactive, make the formation of the adduct M^{2+}L·SOCl$_2$ with relative diffi-

culty; the compounds $(M^{2+}L)$ whose central metal ions of electronic configuration d^5 and d^8, exhibit relatively high catalytic activity as a result of the strong trend to form square planar complexes during the decomposition of $[M^{3+}L\cdot SOCl_2]^+$ and $[M^+L\cdot SOCl_2]^-$, respectively. According to the result, we predict that the MPc derivatives whose central metal ions, such as Cr^{2+}, of electronic configuration d^4, are inactive to Li/SOCl$_2$ battery, whereas the MPc derivatives whose central metal ions, such as Zn^{2+}, of electronic configuration d^{10}, exhibit excellent catalytic activity to Li/SOCl$_2$ battery. This prediction will be confirmed in our further work.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2009.06.047.

References

[1] M. Stantney, W. Ham, Chem. Rev. 104 (2004) 4271–4301.
[2] R.M. Spotnitz, G.S. Yeduvaka, G. Nagasubramanian, R. Jungst, J. Power Sources 163 (2006) 578–583.
[3] L. Qiu, Y.X. Tan, R.Z. Qiu, Z.M. Zhang, Y.L. Du, J.G. Wang, J. Power Sources 54 (1995) 127–133.
[4] K. Chung, J.S. Lee, Y.O. Ko, J. Power Sources 140 (2005) 376–380.
[5] D. Carmier, C.V. Guterl, J. Lahaye, Carbon 39 (2001) 2187–2193.
[6] G.T.K. Fey, M. Hsieh, Y.C. Chang, J. Power Sources 97/98 (2001) 606–609.
[7] M. Kimura, T. Kuroda, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, Langmuir 19 (2003) 4825–4830.
[8] N. Nishiyama, A. Iriyama, W.D. Jang, K. Miyata, K. Itaka, Y. Inoue, H. Takahashi, Y. Yanagi, Y. Tamaki, H. Koyama, K. Kataoka, Nat. Mater. 4 (2005) 934–940.
[9] A. Sorokin, J.L. Séris, B. Meunier, Science 268 (1995) 1163–1166.
[10] K.M. Abraham, M. Alamgir, E.B. Willstaedt, W.P. Kilroy, J. Power Sources 45 (3) (1993) 343–352.
[11] S.B. Lee, S.I. Pyun, E.J. Lee, Electrochim. Acta 47 (2001) 855–864.
[12] N. Doddapaneni, Proceedings of the Symposium on the Chemistry and Physics of Electrocatalysis, The Electrochem. Soc. Inc., Pennington, NJ, 1994, p. 630.
[13] P.A. Bernstain, A.B.P. Lever, Inorg. Chem. 29 (1990) 608–616.
[14] W.S. Kima, Y.K. Choi, Appl. Catal. A 252 (2003) 163–172.
[15] W.S. Kim, W.J. Sim, K. Chung, Y.E. Sung, Y.K. Choi, J. Power Sources 112 (2002) 76–84.
[16] W. Massa, Z. Anorg. Allg. Chem. 633 (2007) 690–692.
[17] C.F. Schwenk, B.M. Rode, CHEMPHYSCHEM 4 (2003) 931–943.