ments).

The instrumental data of PPP obtained from FTIR, XRD, and TA are well agreed with those of Kovacic. From the result of SEM showing in Figure 1, the particle diameter of PPP is about 10 μm, but irregularly large particles are observed, too. As PPP particles have weak cohesive property, it is difficult to make their size be uniform. The chromatograms for the separation of C_{60} and C_{70} in PPP/toluene system are plotted in Figure 2. In Figure 2a, the retention time of air[18] and C_{60} at the flow rate of 70 ml/min is 7 and 20 minutes respectively. In Figure 2b, retention time of C_{70} is 48 minutes and the impurity peak of C_{60}[17] in C_{70} is also obserbed. The resolution capacity factor of C_{70} is about 3 times higher than that of C_{60}, so the chromatogran of C_{70} is much broader than that of C_{60}. Figure 2c shows the separation of C_{60} from C_{70} in its mixture. The retention times of C_{60} and C_{70} in the mixture are exactly the same as those of individual compound, that is, 20 and 48 min respectively. The complete separation of C_{60} and C_{70} with the resolution of about 1.5 was achieved. And C_{70} is retained over twice longer than C_{60}. As mentioned above, it is anticipated that the spherical C_{60} seems to elute faster than ellipsoidal C_{70} in the present chromatographic condition. It is, however, insufficient to describe the retention mechanism of fullerenes in this system. We hope to perform more detailed investgation for the separation mechanism in further study.

Note that our experimental conditions were not optimized for the separation of fullerene in the standard mixture or in the toluene extracts. However the separation ability preliminarily reported here was found to be superior to the existing methods at least by obtaining complete separation of C_{60} and C_{70} with pure toluene solvent. Clearly, this method could separate larger quantities of raw material from the toluene extracts rapidly using much smaller volume of solvent. Additionally, because the pressure of this system was selected at 100 psi, it is possible to make to pump free system.[19] In the condition of high-pressure packing of PPP, the separation efficiency could be significantly improved.

In conclusion, based on the ideas and data described above, the PPP/toluene system promises a strong possibility that can be used for the separation method of fullerene in toluene extracts. This system can also be extended into a preparatory scale and be an alternative for the conventional activated charcoal/toluene system due to its high separation ability of C_{70}

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References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
2. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature*, **347**, 354-358 (1990).
3. P. M. Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Am. Chem. Soc.*, **113**, 2780 (1991).
4. I. C. Jeon, S. H. Kim, J. G. Choi, G. H. Lee, S. Y. Hwang, and S. S. Kim, *Bull. Kor. Chem. Soc.*, **13**, 346 (1992).
5. R. C. Haddon, L. F. Schneemeyer, J. V. Waszcak, S. H. Glarum, R. Tycko, G. Dabbagh, A. R. Kortan, A. J. Muller, A. M. Mujsce, M. J. Rosseinsky, S. M. Makmhija, F. A. Thiel, K. Raghavachari, E. Cockayne, and V. Elser, *Nature*, **350**, 46 (1991).
6. M. S. Meier and J. P. Selegue, *J. Org. Chem.*, **57**, 1924 (1992).
7. R. Tayler, J. P. Hare, A. D. Abdul-Sada, and H. W. Kroto, *J. Chem. Soc., Chem. Commun*, 1423 (1990).
8. A. S. Koch, K. C. Khemani, and F. Wudl, *J. Org. Chem.*, **56**, 4543 (1991).
9. P. Bhyrappa, A. Penicaud, M. Kawamoto, and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, 936 (1992).
10. K. Chatterjee, D. H. Parker, P. Wurz, K. R. Lykke, D. M. Gruen, and L. M. Stock, *J. Org. Chem.*, **57**, 3253 (1992).
11. K. C. Khemani, M. Prato, and F. Wudl, *J. Org. Chem.*, **57**, 3254 (1992).
12. A. M. Vassallo, A. J. Palmisano, L. S. K. Pang, and M. A. Wilson, *J. Chem. Soc., Chem. Commun.*, 60 (1992).
13. W. A. Scrivens, P. V. Bedworth, and J. M. Tour, *J. Am. Chem. Soc.*, **114**, 7917 (1992).
14. Of course, graphite and active charcoal are also another example of this type compound.
15. As far as we know, The use of PPP as a stationary phase in liquid chromatography has not been reported yet.
16. P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).
17. The standard solutions were made using conventional separation method of alumina/hexane system. In general, the C_{70} solution obtained from this technique, contains about 5% of C_{60} as impurities due to incomplete separation of fullerene.
18. When the solvents has been used as mobile phase, in order to make the reference peak, the air was injected with sample using the injection valve.
19. 100 psi is the obtainable pressure from conventional N_2 regulator. So ordinary nitrogen tank could substitute the expensive high pressure pump.

Effect of Fe(II)-Tetradentate Schiff Base Complex on the Electrochemical Reduction of Thionyl Chloride

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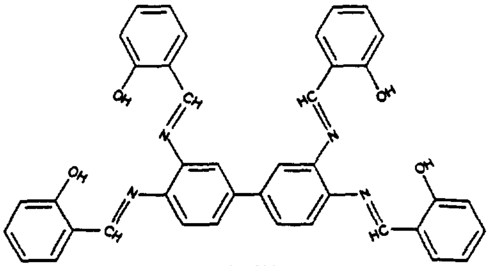
The lithium thionyl chloride system has emerged as one of the best primary batteries having combined characteristics of high rate capability, high energy density, long shelf life, and efficient low temperature operation. The electrochemical reduction of thionyl chloride has been studied extensively due to its importance in high power density primary batteries based on the Li-$SOCl_2$ chemistry[1-11]. At the cathode surface, the electrochemical reduction of thionyl chloride takes place and depends strongly on the cathode material. The electrode kinetics for the cathode discharge reaction is rather poor due to the formation of the passive LiCl films at the cathode as a result of the reaction.

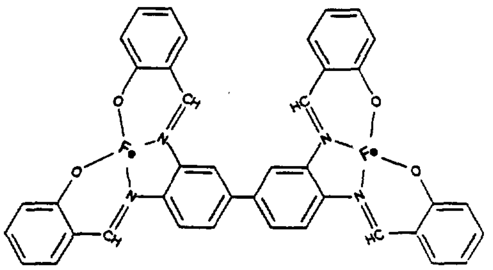
$$2SOCl_2 + 4e^- \rightarrow SO_2 + S + 4Cl^-$$

One approach to enhance the cell performance could be the addition of catalyst molecules, which make the rate of electron transfer faster. It has been shown by several investigators[12-17] that adding a small amount of metal phthalocyanines improves cell performance by improving both thermodynamic and kinetic parameters for the thionyl chloride reduction.

In this report, we describe the effect of Fe(II) tetradentate schiff base complex on the reduction of thionyl chloride by evaluating electronic parameters involved. A quadridentate schiff base ligand, 3,3', 4,4'-tetra(salicylidene imino)-1,1'-biphenyl ($TSBPH_4$) was prepared by a well established method[18]. A 5 mM 3,3'-diaminobenzidine solution in methanol was slowly added to the same volume of 10 mM salicylaldehyde in methanol under the nitrogen atmosphere. When the mixed solution was slowly stirred, a reddish yellow precipitate was recrystallized in methanol and dried under reduced pressure at 80℃. $Fe(II)_2$-TSBP·$4H_2O$ was then prepared by adding 1 mM $TSBPH_4$ in methanol to the same volume of 2 mM $Fe(NO_3)_2 \cdot 6H_2O$ in methanol slowly while stirring under the nitrogen atmosphere. A dark brown precipitate obtained was then recrystallized from methanol and dried at 80℃ under reduced pressure. Yield: 93% Elemental analysis(%): C=59.8, H=3.89, N=7.07, H_2O=8.14, Fe=14.21 (Cal. C=59.29, H=3.73, N=6.91, H_2O=8.89, Fe=13.78); UV-vis (DMF, λ_{max}, $\varepsilon \times 10^{-4}$ $cm^{-1}M^{-1}$): 412 (1.23), 492 (0.75); IR (KBr, cm^{-1}): 3041, 1607, 1437, 1250, 1198, 1034, 842, 675, 570; T.G.A. (weight loss, %); 100-210℃ =7.32, 210-871℃ =70.31, 871℃ - =22.37. The results agree well with predicted compositions of the proposed complex, Also, the content of iron is in excellent agreement with the proposed complex of one base molecule with two metal atoms.



TSBPH₄



(Fe)₂(TSBP)

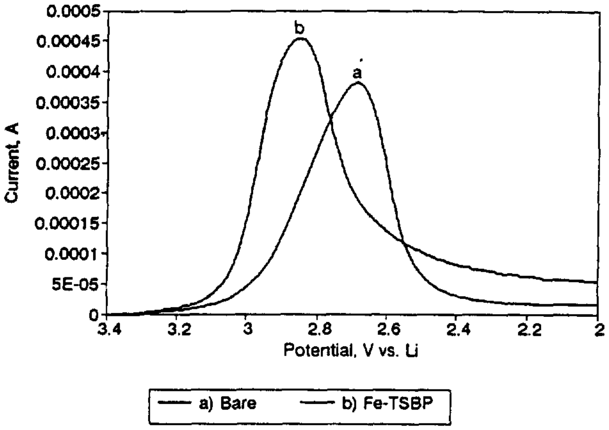


Figure 1. Cyclic voltammograms recordered at the glassy carbon electrode for the reduction of the $SOCl_2$ solution containing a) 0 and b) 0.61 mM Fe(II)-TSBP. Scan rate was 50 mV/s.

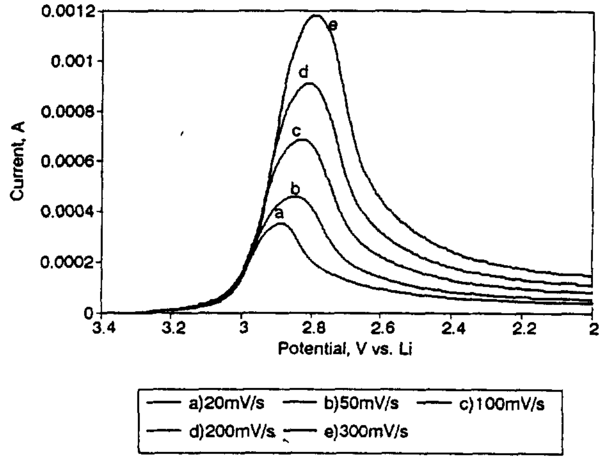


Figure 2. Scan rate dependency of the Cyclic Voltammograms (CV) recorded at the glassy carbon electrode for the $SOCl_2$ solution containing 0.61 mM Fe(II)-TSBP. Scan rate were a) 20, b) 50, c) 100, d) 200, and e) 300 mV/s, respectively.

Electrochemical reduction of thionyl chloride has been carried out by cyclic voltammetry techniques. A single compartment cell, in which a glassy carbon (geometric area, 0.071 cm^2) working, a molybdenum wire counter, and a lithium wire reference electrodes are housed, was used for this study. Aldrich's thionyl chloride, aluminum chloride, and Johnson-Mattey's lithium chloride were used to make up a 1.5 M $LiAlCl_4$ solution in thionyl chloride. Solutions were prepared in a glove box in an Ar-gas atmosphere. A Princeton Applied Research (PAR) 273 potentiostat/galvanostat was used for recording cyclic voltammograms. For a detailed investigation of the effect of schiff base complex on $SOCl_2$ reduction, this process was studied in solutions containing Fe(II)-TSBP.

Figure 1 shows cyclic voltammograms on glassy carbon without additive and in the presence of Fe(II)-TSBP. As can be seen from Figure 1, the reduction of $SOCl_2$ in the absence

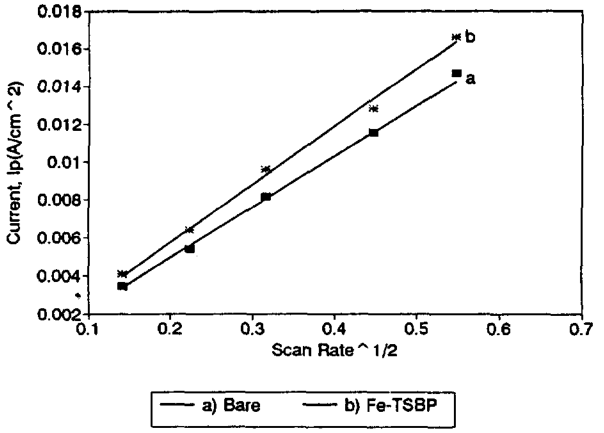


Figure 3. Plots of CV peak current *vs.* $v^{1/2}$ at the glassy carbon electrode for the reduction of the $SOCl_2$ solution containing a) 0 and b) 0.61 mM Fe(II)-TSBP.

of additive is described by a curve with a clearly defined current maximum i_p at the potential E_p of about 2.684 V *vs.* Li. The current drop at less positive potentials seems to be due to passivation of the electrode by lithium chloride[19]. Introduction of 0.61 mM Fe(II)-TSBP complex into the net $SOCl_2$ solution (13.71 mole/*l*) leads to an increase of the maximum peak current i_p. In the presence of Fe(II)-TSBP, the catalytic effect is clearly seen as shown by the positive shift in the potential for thionyl chloride reduction and an increase in cyclic voltammetric peak current. Enhancement in power density of 130% is noted for the glassy carbon electrode. Figure 2 shows voltammograms in the presence of 0.61 mM Fe(II)-TSBP at different scanning rates v. The dependence of i_p on $(v)^{1/2}$ for solutions without and with Fe (II)-TSBP addition (Figure 3) are both linear, but differ in slope. In this result, significent improvement in cell performance is noted in terms of exchange rate constant of up to 10 times. Most of the enhancement originates from improvements in apparent diffusion coefficient and exchange rate constant in thionyl chloride solution containing catalyst.

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References

1. C. R. Schlaikjer, F. Goebel, and N. Marincic, *J. Electrochemical. Soc.*, **126**, 513 (1979).
2. W. Bowden and A. N. Dey, *ibid.*, **126**, 2035 (1979).
3. N. Doddapaneni, *Proc. 30th Power Source Symposium,* the Electrochemical Society, Pennington, NJ. (1982).
4. W. K. Istone and R. J. Brodd, *J. Electrochem. Soc.*, **129**, 1853 (1982).
5. W. K. Istone and R. J. Brodd, *J. Electrochem. Soc.*, **131**, 2467 (1984).
6. M. J. Madou and S. Szpak, *ibid.*, **131**, 2471 (1984).
7. W. P. Hagan, N. A. Hampson, and P. K. Packer, *Electrochim. Acta,* **31**, 699 (1986).
8. M. J. Madou, J. J. Smith, and S. Szpak, *J. Electrochem. Soc.*, **134**, 2794 (1987).
9. A. J. Hills and N. A. Hampson, *J. Power Sources,* **24**, 253 (1980).
10. P. A. Mosier-Boss, S. Szpak, J. J. Smith, and R. J. Nowak, *J. Electrochem. Soc.*, **136**, 2455 (1989).
11. V. S. Vag Sky, V. E. Kazarinov, Yu. M. Volfkovich, L. S. Kanevsky, and L. A. Beketayeva, *J. Power Sources,* **26**, 427 (1989).
12. N. Doddapaneni, *Proc. 30th Power Symp.*, 169 (1982).
13. N. Doddapaneni, *Proc. 30th Power Symp.*, 411 (1984).
14. N. Doddapaneni, *Proc. Sysmp. Lithium Batteries,* **84-1**, 122 (1984).
15. N. Doddapaneni, *Proc. Electrochem. Soc.*, **86-12**, 630 (1986).
16. N. Doddapaneni, *Proc. 32nd Power Symp.*, 525 (1986).
17. P. A. Bernstein and A. B. P. Lever, *Inorg. Chem.*, **29**, 608 (1990).
18. K. H. Chjo, Y. K. Choi, S. J. Lee, C. Y. Kim, and C. P. Rim, *J. Korean Chem. Soc.*, **36**, 79 (1992).
19. K. Behl, *Proc. 27th Power Sources Symp.*, Atlantic City, The Electrochem. Soc. Inc., Pennington, NJ. 1976, pp. 30-33.

Direct Synthesis of 2,2-Dichloro-2-silaindan

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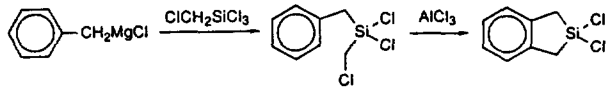
Since the direct synthesis of chloromethylsilanes from metallic silicon and methyl chloride at high temperature around 300℃ was discovered by Rochow,[1] direct reactions of metallic silicon with various alkyl chlorides have been studied extensively.[2] However, the direct reaction of benzyl chloride with silicon has not been reported yet, because benzyl chloride decomposes rapidly when contacted with Si-Cu contact mixtures at temperature above 150℃.[3] We have attempted the direct reaction of metallic silicon with α,α'-dichloro-*o*-xylene having two benzylic chlorides within the molecule. 2,2-Dichloro-2-silaindan is expected to be prepared directly from metallic silicon and α,α'-dichloro-*o*-xylene. Alkyl-2-silaindanes are known to undergo a ring opening polymerization and the resulting polymers have high melting temperature and thermal stability.[4] Therefore, 2,2-dichloro-2-silaindan is a strong candidate as a starting material for the ring opening polymerization. Until now 2,2-dichloro-2-silaindan (I) has only been prepared in multiple steps using various techniques such as Grignard and Friedel-Crafts reactions as following.[5]



I

We wish to report here in the first preparation of **I** by directly reacting metallic silicon with α,α'-dichloro-*o*-xylene