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 C60 and C70 in PPP/toluene system are plotted in Figure 2. In Figure 2a, the retention time of air14 and C60 at the flow rate of 70 ml/min is 7 and 20 minutes respectively. In Figure 2b, retention time of C60 is 48 minutes and the impurity peak of C6017 in C70 is also observed. The resolution capacity factor of C60 is about 3 times higher than that of C70, so the chromatogram of C60 is much broader than that of C70. Figure 2c shows the separation of C60 from C70 in its mixture. The retention times of C60 and C70 in the mixture are exactly the same as those of individual compound, that is, 20 and 48 min respectively. The complete separation of C60 and C70 with the resolution of about 1.5 was achieved. And C70 is retained over twice longer than C60. As mentioned above, it is anticipated that the spherical C60 seems to elute faster than ellipsoidal C70 in the present chromatographic condition. It is, however, insufficient to describe the retention mechanism of fullerene in this system. We hope to perform more detailed investigation 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 C60 and C70 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.10 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 C70.

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References

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.
17. The standard solutions were made using conventional separation method of alumina/hexane system. In general, the C70 solution obtained from this technique, contains about 5% of C60 as impurities due to incomplete separation of fullerene.
18. When the solvent 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 N2 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-SOCl₂ chemistry. 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.

2SOCl₂ + 4e⁻ → SO₂ + 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 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) tetradequate 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 (TSBPH₄) was prepared by a well established method. 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°C. Fe(II)-TSBP·4H₂O was then prepared by adding 1 mM TSBPH₄ in methanol to the same volume of 2 mM Fe(NO₃)₃·9H₂O in methanol slowly while stirring under the nitrogen atmosphere. A dark brown precipitate obtained was then recrystallized from methanol and dried at 80°C under reduced pressure. Yield: 95% Elemental analysis(%): C = 59.8, H = 3.89, N = 7.07, Fe = 14.21 (Cal. C = 59.20, H = 3.73, N = 6.91, Fe = 13.78); UV-vis (DMF, λ_max, ε×10⁻⁴ cm⁻¹ M⁻¹): 412 (1.23), 492 (0.75); IR (KBr, cm⁻¹): 3041, 1607, 1437, 1250, 1198, 1034, 842, 575, 570; T.G.A. (weight loss, %); 100-210°C = 7.32, 210-871°C = 70.31, 871°C = 22.37. The results agree well with the proposed complexes of the proposed complex.

Also, the content of iron is in excellent agreement with the proposed complexes of one base molecule with two metal atoms.

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 cm²) 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-Mathey's lithium chloride were used to make up a 1.5 M LiAlCl₄ 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 SOCl₂ 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 SOCl₂ in the absence
Figure 3. Plots of CV peak current vs. $v^{1/2}$ at the glassy carbon electrode for the reduction of the SOC12 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. Introduction of 0.61 mM Fe(II)-TSBP complex into the net SOC12 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, significant 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


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°C 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°C.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

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