- d outside diameter of the reference capillary, cm
- Ε cell EMF, V
- i current density, A/cm²
- exchange current density for anodic reaction, A/cm² $i_{0,a}$
- exchange current density for cathodic reaction, $i_{o.c}$ A/cm²
- current path, cm
- S distance between the Luggin capillary tip and the working electrode, cm
- v measured potential, V
- grid spacing in the horizontal direction, cm Δx
- grid spacing in the vertical direction, cm Δy
- empirical correction factor, dimensionless e
- к specific conductivity, S/cm
- activation overpotential, V η_{a}
- mass-transfer overpotential, V η_c
- ohmic overpotential, V η_{Ω}

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The electrochemistry of SOCl₂ reduction has received considerable attention because of its relevance to the performance and safety of Li/SOCl₂ high energy density batteries. The overall electroreduction proceeds as follows

$$Li + 2SOCl_2 \rightarrow 4LiCl + SO_2 + S$$
 [1]

The salt LiAlCl₄ is used for ionic conductivity.

Recent studies have shown evidence for formation of free radical intermediates or side reaction products using electron spin resonance spectroscopy (1, 2). These species are long lived, although probably in low concentration. Cyclic voltammetry studies have shown that there are no concentrated soluble intermediates with lifetimes between 0.1 and 48h (3).

The application of Raman emission spectroscopy has revealed the existence of LiAlCl4 donor-acceptor complexes with SO₂ and SOCl₂ (4) and their importance to the reduction of $SOCl_2$ (1). Practical Raman measurements of $SOCl_2$ reduction in situ in small quartz electrochemical cells were plagued by a broad fluorescence when solutions were excited with an argon laser at 514.5 nm.

The ultraviolet/visible spectroscopy of oxyhalides has received some attention from chemists over the years. For instance POCl₃ was shown to enhance fluorescence of steroids by as much as seven-fold without shifting the wavelength maxima of emitted light (5). Complexes of SOCl₂ and AlCl₃ create strong charge transfer complexes with aromatic solvents (6), while Dey has demonstrated the usefulness of ultraviolet/visible absorbance spectroscopy in

following the electroreduction of SOCl₂ in acetonitrile, $N(C_4H_9)_4PF_6$ supporting solvent (7).

The present investigation was initiated to determine a more suitable excitation wavelength for future Raman spectroscopy and to characterize the fluorescence resulting from SOCl₂ electroreduction.

Experimental

Solutions of reduced SOCl₂ were prepared in two ways: (i) electrochemical reduction in practical Li/SOCl₂ cells using Teflon-bonded carbon cathodes and (ii) electrochemical reduction on molybdenum foil in direct contact with metallic lithium.

Procedure 1 was carried out using sealed low rate Li/SOCl₂ cells with porous, approximately 0.25 in. thick, Teflon-bonded carbon cathodes and lithium anodes in sealed stainless steel containers. These cells used glass separator material (Crane Company) and Nickel 200 current collectors and were discharged at 1 mA/cm² of geometric surface area.

Procedure 2 was carried out in sealed 1 cm fluorimeter cuvettes (Starna Company Spectrosil Grade Quartz). SOCl₂ reduction proceeded slowly driven by galvanic corrosion

The SOCl₂ electrolyte solutions contained 1.8M LiAlCl₄, unless otherwise noted, and contained less than 20 ppm water equivalents as measured by infrared spectrometry (8). Traces of SO₂Cl₂, Cl₂, SCl₂, and S₂Cl₂ were removed by refluxing. In each experiment, the extent of SOCl₂ reduction is expressed in terms of equivalents reduced per liter of initial solution volume. This convention is necessary be-

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cause of the change in solution volume during discharge.

Molybdenum foil was chosen as a surface for galvanic reduction of SOCl₂ by lithium because of its stability in SOCl₂ electrolytes (9). This small cell contained in a quartz cuvette provided an opportunity to study the reduction of SOCl₂ in the complete absence of traces of metals and organics which might interfere spectroscopically.

All fluorescence measurements were carried out in either flame-sealed 1 mm borosilicate capillaries or 1 cm quartz Spectrosil Cuvettes (Starna Company) sealed with snug fitting Teflon caps.

The majority of the fluorescence emission measurements were carried out in a Hitachi-Perkin-Elmer MPF-2A Spectrometer. Solutions were excited with a xenon lamp (Osram No. XBO 150W). Excitation spectra were collected on a Spex Fluorolog because of its ability to compensate for the xenon lamp emission spectra. Absorption spectra were collected using a Perkin-Elmer Lambda 3B Spectrophotometer.

Results

Discharged solutions of SOCl₂ electrolyte show broad fluorescent emissions over the range of 450-650 nm, characteristically trailing off at higher wavelengths. Figure 1 compares the fluorescence spectra of briefly discharged electrolyte (0.33 equiv. SOCl₂/liter electrolyte) from Li/ SOCl₂ cells with that of the 1.8M fresh electrolyte. The excitation wavelength was 500 nm. Figure 1 also shows the spectrum of a solution made up to approximate the discharged electrolyte from Eq. [1]: 1.8M LiAlCl₄, 0.3M SO₂, 0.2M sulfur and saturated with LiCl.

In order to be certain that the observed fluorescence was not related to traces of organic or metal contaminants in



WAVELENGTH (nm)

Fig. 1. Fluorescence spectra in SOCI₂: (A) 2% discharged electrolyte; (B) galvanically reduced electrolyte on molybdenum foil; (C) 1.8M LiAICI₄, 0.2M sulfur, 0.3M SO₂, LiCl saturated; and (D) 1.8M LiAICI₄. the carbon cathode cells, $SOCl_2$ was reduced using the lithium on molybdenum galvanic cells. After only 14 days, there was sufficient electroreduction of $SOCl_2$ to produce fluorescence (Fig. 1). The fluorescence of undischarged 1.8M LiAlCl₄ in $SOCl_2$ is shown for comparison. No emission was detected for $SOCl_2$ alone.

Electrolyte from extensively discharged electrolyte (16 equiv. $SOCl_2$ reduced/liter of initial solution) yields a fluorescence intensity approximately equal to that of briefly discharged electrolytes.

Ultraviolet/visible absorbance spectra of reduced electrolyte, simulated discharged electrolytes, 1.8M LiAlCl₄ undischarged electrolyte, and neat SOCl₂ are shown in Fig. 2. A prominent shoulder at 440-540 nm appears on reduction of SOCl₂ in addition to the strong solvent absorption below 390 nm.

Lastly an attempt was made to characterize the excitation spectrum of reduced $SOCl_2$. Using an emission wavelength of 600 nm, a scan of the excitation wavelength showed a broad maximum at 500 nm with a distinct shoulder at 430 nm.

Discussion

The intense fluorescence produced in electrochemically reduced solutions of $SOCl_2$ is 2-4 times that of fresh solutions of LiAlCl₄ in $SOCl_2$, with maxima shifted to slightly higher wavelengths. The weak fluorescence in the unreduced solutions indicates that the LiAlCl₄ · 2SOCl₂ molecular complex identified with Raman and infrared (1, 4), behaves like a charge transfer complex. Elemental sulfur and SO_2 dissolved in undischarged electrolyte do not fluoresce. Thus, the greatly enhanced fluorescence of reduced SOCl₂ suggests an additional charge transfer complex formed between LiAlCl₄ and a by-product of SOCl₂ reduction. This strong fluorescence is observed in electrolyte from discharged cells even after a year of storage.

The fluorescence quantum efficiency of this species must be relatively high, since a brief discharge in the galvanic couple cell produced a noticeable emission. The species may be present in relatively small quantities and may or may not be present in proportion to the amount of reduced SOCl₂.

The extensively reduced solution fluoresces only slightly more than the briefly discharged solution. In a separate experiment, the briefly discharged solution was diluted ten-fold with SOCl₂. This produced only a two-fold



WAVELENGTH (nm)

Fig. 2. Absorbance spectra in SOCI₂: (A) 100% discharged electrolyte; (B) 2% discharged electrolyte; (C) galvanically reduced electrolyte on molybdenum foil; (D) 1.8M LiAICI₄, 0.2M sulfur, 0.3M SO₂, LiCl saturated; (E) 1.8M LiAICI₄; and (F) neat SOCI₂.

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reduction in intensity but shifted the maximum to a lower wavelength. Furthermore, the fluorescence intensity of the reduced solution was quite sensitive to optical path. Back fluorescence from the face of the cuvette was stronger than that measured with a 90° path through the cell. These observations together indicate that the fluorescence intensity observed is not directly proportional to concentration so that fluorescence quenching and/or inner filter effects are likely.

The shoulder for the absorption spectra of discharged electrolyte at 500 nm is close to the maximum in the wavelength excitation scan at 510 nm. It therefore appears, that a single species accounts for both features and for the strongly enhanced fluorescence at 550-600 nm.

Electron spin resonance studies in dimethylformamide show that at SO_2 concentrations above 0.05*M*, a single free radical species, $(SO_2)SO_2^-$, is produced during the controlled one-electron reduction of SO_2 (10). Using spectroscopy, ultraviolet-visible this free radical dimer has been associated with a strong absorption at 580 nm in this solvent (11). Furthermore, electrochemical studies have shown that this dimer is stable in acetonitrile and hexamethylphosphoramide (12), amide solvents (13), n-methylpyrrolidinone (14), and even metastable in water (15). It is, therefore, tempting to assign the absorption of 500 nm and resultant fluorescence in electroreduced $SOCl_2$ to $(SO_2)SO_2^-$ dimer. Electron spin resonance measurements of reduced SOCl₂ electrolyte support the existence of at least one free radical species stable in the $LiAlCl_4$ - $SOCl_2$ - SO_2 media (1, 2).

On the other hand, a strong Raman emission at 1081 cm^{-1} detected for (SO₂)SO₂⁻ generated in DMF (13) is absent in Raman spectra of extensively discharged Li/SOCl₂ electrolyte, although it may account for the infrared absorption at 1070 cm⁻¹ occurring in freshly discharged SOCl₂ (1).

Positive identification of the fluorescing species must await careful correlation of electron spin resonance, Raman, fluorescence, and voltammetry results in SOCl₂ and supporting solvents. Current efforts in this laboratory are focusing on the stability of the fluorescence and its dependence on exciting wavelengths and electrolyte salt.

The technique of fluorescence spectroscopy offers promise in the search for a more complete picture of the chemical and electrochemical reactions of SOCl₂. The complex optical interaction between absorption, excitation, and fluorescence in these solutions offers a challenge in arriving at a correct interpretation.

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A Technique for Delineation of PN Junctions in Cubic Silicon Carbide

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Recently, cubic silicon carbide has been receiving a tremendous amount of attention in the semiconductor world (1-3). Its large bandgap, high saturation velocity, radiation hardness, and relatively large low field mobility are just a few of its properties which make it a candidate for high temperature radiation resistant semiconductor devices. Kondo and co-workers (4) have reported on SiC MESFET devices. If continued improvements are to be made on these and other devices, it must be possible to control and measure junction depth to within a few hundred angstroms. In this technical note, we briefly describe a

highly precise technique for delineating pn junctions in beta SiC grown on silicon substrates.

Experimental Discussion

The epitaxial SiC layers used for the development of this technique were grown at 200 torr by reacting propane (C_3H_8) and silane (SiH₄). The growth temperature was approximately 1343°C and a carbonized layer of SiC was used to reduce the strain at the interface between the SiC and silicon. A complete description of this process and the CVD system is provided by Harris (5). The p-type dopant