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1991

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Prospects for Using C₆₀ and C₇₀ in Lithium Batteries

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ABSTRACT

Solid films of C₆₀ and C₇₀ fullerenes are evaluated in propylene carbonate/lithium perchlorate, an electrolyte commonly used in lithium batteries. Cyclic voltammetry, chronopotentiometry, and an effusion test, show that reduced C₆₀ and C₇₀ are soluble in the electrolyte tested, which, coupled with poor stability of the highly reduced material and poor electrochemical reversibility, would compromise the performance of secondary batteries based on these fullerenes.

Immediately following the recent synthesis of macroscopic amounts of C₆₀ and other fullerenes (1), the electrochemical reduction of these materials was found to be highly reversible (2, 3), prompting the suggestion that fullerenes might be employed as novel materials for rechargeable batteries. Since the reduced fullerenes are sensitive to ambient, it is reasonable to suppose that they would be used in organic electrolytes, particularly in conjunction with lithium to maximize energy density. Other carbon- or organic-based electrodes, such as graphite (4) and electrically conducting polymers (5), have been employed in lithium batteries with varying degrees of success. C₆₀ can be reduced to the extent of five electrons per molecule, although reduction beyond C₆₀³⁻ is observed to be rather irreversible (3, 6), thereby limiting the maximum energy density that is to be expected from this material. Nevertheless, it is of interest to explore the fullerenes in the context of present battery technology.

Early cyclic voltammetry (CV) studies (2, 3) were done on dilute solutions of fullerenes. A solid morphology is preferable for battery applications, and Jehoulet *et al.* very recently published the first CV studies of solid C₆₀ reduction in acetonitrile (6), a solvent which is not compatible with lithium. We report here cyclic voltammetry and constant-current discharge experiments on C₆₀ and C₇₀ in propylene carbonate/lithium perchlorate electrolyte, with the objective of evaluating these new materials as candidates for lithium batteries.

The fullerenes used for our experiments were extracted from enriched soot (Texas Fullerenes) and purified chromatographically according to the literature (3). Thin films were deposited from toluene onto platinum foil electrodes. The electrolyte used for this study was 0.5M LiClO₄ (Aldrich, dried under vacuum at 180°C) in propylene carbonate (Aldrich, vacuum distilled from CaH₂). Electrochemistry was performed exclusively in a dry box. The cyclic voltammetry of C₆₀ and C₇₀ in these solvents is shown in Fig. 1. There are similarities to the results of Jehoulet *et al.*, as well as significant differences. The reductions are not as well resolved as those in acetonitrile, and the first cathodic peak is larger than subsequent peaks. For C₆₀, the shapes of the subsequent peaks are similar, though the magnitude continues to decrease with cycling. For C₇₀, three reductions are resolved on the first scan and subsequent cycles have a markedly different appearance. The electrochemistry of solid fullerenes appears to be considerably less reversible than that of dissolved fullerenes. Though the anodic peaks for reoxidation of C₆₀ and C₇₀ ions appear to be at the same position (2.49 and 2.17 V vs. Li) the reduction of C₇₀ occurs at a less-negative potential. If resistance changes in the films are important during cycling (6), it may be that the C₇₀ is less resistive in the neutral state, yielding less hysteresis between forward and reverse peaks. Gottesfeld *et al.* have recently shown (7) that resistance changes in modified electrodes can induce hysteresis in cyclic voltammetry.

As shown above, the electrochemical response is not stable to cycling. We have performed reductions on larger, milligram quantities of C₆₀ and have found that, whereas the neutral fullerene is not soluble in the electrolyte, the fulleride anion is soluble. This behavior is not apparent on the thin film samples. It thus appears that one of the main reasons for loss in electroactivity of C₆₀ coated electrodes occurs through solubilization of the electroactive material, an undesirable property for lithium batteries. To illustrate this phenomenon, a small amount, 3.4 mg, of powdered C₆₀ was sandwiched between a platinum disk and a 0.4 μm pore-size filter membrane using an electro-

chemical doping cell described previously (8). The assembly, including the C₆₀, was immersed in electrolyte. No coloration was observed, consistent with the insolubility of neutral C₆₀ in propylene carbonate. A voltage of 2.0 V vs. Li was then applied to the sample. The highly colored reduced C₆₀ was observed to effuse through the filter membrane and into the bulk electrolyte. The UV-vis spectrum of the resulting solution showed a peak at 330.5 nm, closer to the adsorption maximum for C₇₀ than C₆₀, Ref. 9. (We believe the small quantities of electro-generated C₆₀⁻ ions were converted back to C₆₀ by impurities introduced as a result of sample handling and transfer to the UV-vis cuvette). Jehoulet *et al.* (6) observe that the electrochemical response in their system is more stable when large tetraalkylammonium cations are employed. It is possible that reduced C₆₀ is insoluble in the presence of these ions.

While the cathodic peaks in the CVs are not well resolved, it was observed that the charge on the first reduction was consistently 10-50% lower than expected from the mass of material deposited on the electrode. Electron micrographs showed that C₆₀ and C₇₀ were deposited as crystallites a few micrometers in dimension. It is possible that unreduced fullerene could be lost from the electrode surface by detachment of these crystallites during reduction.

The loss in electroactivity of fullerenes is further manifested by constant-current cycling, which simulates more closely the expected behavior in lithium batteries. Figure 2 depicts reduction followed by re-oxidation at 13.3 (C₆₀) and 11.5 (C₇₀) A g⁻¹ constant current. The potential decreases in a relatively featureless fashion over the range studied, corresponding to a nominal 3 electrons per fullerene molecule on the first discharge, consistent with the poorly-resolved CV. The recharging cycle only reoxidizes ca. 60% of the reduced material, and

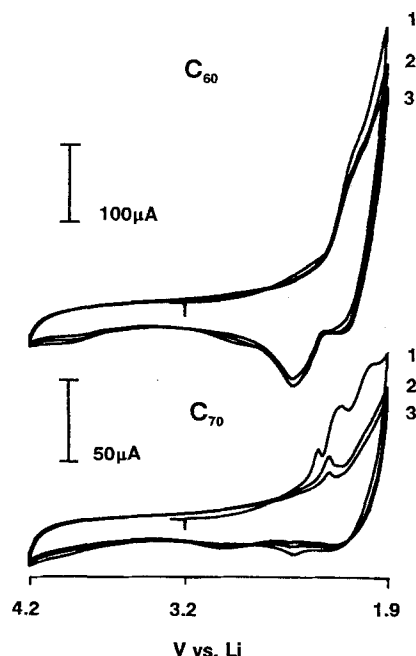


Fig. 1. Cyclic voltammetry of C₆₀ and C₇₀ on Pt foil in 0.5M LiClO₄/propylene carbonate at 250 mV sec⁻¹ scan rate. First three cycles for each is shown. Lithium reference electrode.

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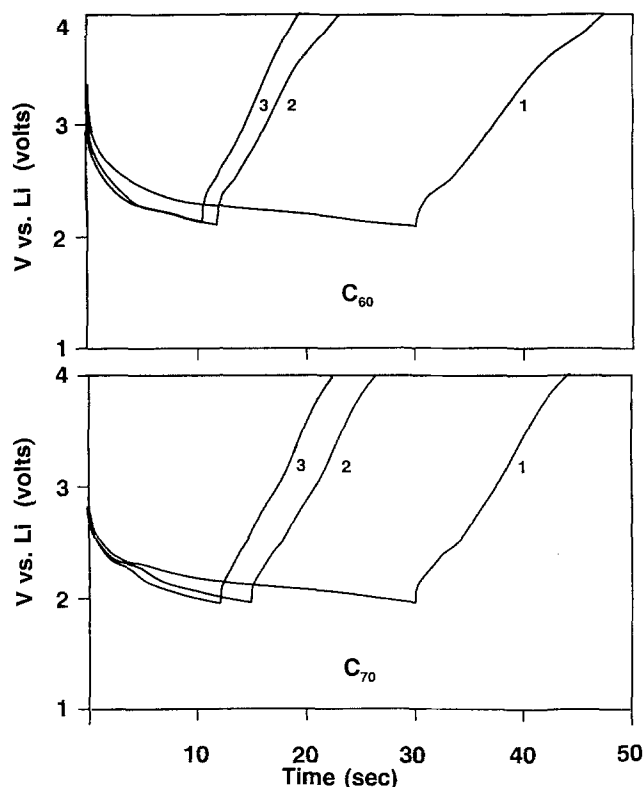


Fig. 2. Constant current reduction and oxidation of C_{60} ($4.4 \mu\text{g}$ at $59 \mu\text{A}$) and C_{70} ($3.6 \mu\text{g}$ at $41 \mu\text{A}$) in $0.5\text{M LiClO}_4/\text{propylene carbonate}$, lithium reference. First three discharge/charge cycles are shown. 30 seconds corresponds to three electrons per molecule.

subsequent discharge cycles to the same potential involve progressively less charge, see Fig. 2. The upper limit for oxidation was chosen to be 4.0 V , where irreversible oxidation of neutral C_{60} begins (6). The large differences in potential for charging and discharging imply inefficient energy storage.

The solubility of reduced fullerenes in propylene carbonate does not bode well for applications to lithium batteries. Though it may be possible to find counterions which form an insoluble product with fulleride ions, one is obviously con-

strained to Li^+ for lithium batteries. There are further observations which have an important impact on the potential for use of fullerenes. The addition to C_{60} of more than three electrons appears to be a chemically irreversible process. Limiting the reduction of C_{60} to C_{60}^{3-} and employing an average discharge voltage of 2.0 V would give a maximum theoretical energy density (10) of 217 Wh kg^{-1} , which is not a particularly high value. Other advanced inorganic and organic materials for secondary batteries, such as TiS_2 and polyaniline, have maximum theoretical energy densities of ca. 450 and 200 Wh kg^{-1} , respectively (11, 12), and show more efficient cycling and better charge/discharge characteristics.

Manuscript submitted August 5, 1991; revised manuscript received September 10, 1991.

Florida State University assisted in meeting the publication costs of this article.

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Real-Time Measurement of Electrolyte Resistance Fluctuations

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ABSTRACT

An electronic device has been devised in order to measure simultaneously the potential fluctuations and the electrolyte resistance fluctuations of an electrode. The separation of the ohmic and faradaic components of the potential fluctuations allows a more precise identification of the elementary events generating this voltage electrochemical noise (bubble detachment on a gas-evolving electrode, contact between particles in a fluidized electrode, etc.). Transients of the electrolyte resistance as fast as 1 ms can be measured by this device with a precision better than 0.1% .

Noise analysis in electrochemical systems appears to be a suitable method to obtain new information on the dynamic behavior of the system, especially when the voltage (under galvanostatic control) or current (under potentiostatic control) fluctuations are due to elementary events on the electrode involving a large number of molecules or ions: growth and de-

tachment of bubbles on a gas-evolving electrode, or contacts between charged particles in a fluidized bed reactor, or pits in localized corrosion (1-3).

The voltage or current fluctuations produced by these elementary events can be explained in different ways, such as fluctuations of the electrode active surface and fluctuations of the concentrations of the consumed or produced species. Examination of both the time recordings and the power spectral

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