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To cite this article: X. Y. Song *et al* 1996 *J. Electrochem. Soc.* **143** L120

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the devices. An arsenic ion implantation at 80 keV at a dose of 4×10^{15} ion/cm² was used to generate the protrusions. The total length of the protrusions underneath the gate electrode was 40 μ m. The photoresist layer was removed by a combination of 45 min O₂ plasma and 10 min SPM at 80°C. The processing of the samples included a 30 min anneal in N₂ at 900°C, the deglazing of the implantation screening oxide and a pregate cleaning in an FSI mercury spray-post processor. The yield of the capacitors, as defined by the devices that survived stressing fields higher than 12 MV/cm in a ramp-voltage breakdown (E_{BD}) test, is $90 \pm 2\%$ for the reference devices and $89 \pm 2\%$ on the implanted capacitors. It is clear that the presence of the protrusions generated by the ion implantation process in the device gate area does not affect the electrical properties of the 6.5 nm gate oxides and should not cause any degradation of device yield.

Conclusion

It was observed that a high dose ion implantation into patterned photoresist layers resulted in the formation of protrusions at the border of the implanted region. The protrusions have no measurable impact on the gate oxide integrity of 6.5 nm oxides when present in the gate area of the devices. Moreover, they are removed during the recrystallization of the implanted region. However, they prevent the study of the stripping process by sensitive light-scattering

because their scattered signal masks the one from real particles and residues.

Acknowledgment

The authors acknowledge Phillippe Roussel for performing the TEM measurements. A.L.P.R. thanks CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) Brazil, for financial support.

Manuscript submitted Jan. 2, 1996; revised manuscript received Feb. 20, 1996.

Texas Instruments assisted in meeting the publication costs of this article.

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Microstructural Characterization of Lithiated Graphite

X. Y. Song and K. Kinoshita*

Energy and Environment Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

T. D. Tran*

Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California 94550, USA

ABSTRACT

The microstructures of lithiated graphite were studied using high-resolution transmission electron microscopy (HRTEM) and x-ray diffraction (XRD). HRTEM shows lattice images of the (001) layers of LiC₆ with layer spacing of 3.70 Å, consistent with XRD. The morphology and distribution of the LiC₆ and LiC₁₂ phases were investigated by dark field image and selected-area electron diffraction in TEM. The results indicate that LiC₆ and LiC₁₂ phases can coexist in the lithiated graphite particle.

Introduction

Lithium metal has many attractive features as a negative electrode for use in rechargeable lithium batteries. These include its high specific capacity (3862 mAh/g) and high cell voltage when it is used in cells which contain nonaqueous electrolytes (>3 V). Two traditional technological issues with lithium metal in secondary batteries are the limited cycle life and safety concerns. The development of Li-ion batteries avoids the presence of lithium metal by utilizing carbonaceous materials that intercalate lithium ions to form the negative electrode. The viability of this technology is evident by the successful commercialization of Li-ion batteries by Sony Corporation in the early 1990s. Since that time, carbon materials for lithium-ion rechargeable batteries have attracted much attention from both the scientific and industrial communities because of their unusual and useful properties.

Various carbon materials such as graphite, petroleum coke, carbon black, carbon fiber, amorphous carbon, etc., with a wide spectrum of physical and chemical characteristics have been evaluated in Li-intercalation electrodes.¹⁻⁵ In particular, there has been considerable effort^{6,7} spent to investigate graphite in lithium intercalation compounds, Li_xC₆ ($0 \leq x \leq 1$). Its capability of intercalating lithium to $x = 1$ in LiC₆ is equivalent to a gravimetric specific capacity of 372 mAh/g. Structurally, it is generally accepted, based on research by Guerard and Herold,⁸ Kambe *et al.*,⁹ Ohzuku *et al.*,¹⁰ and Zanini *et al.*,¹¹ that the lithium-ion occupation sites are between two adjacent C layer planes where one lithium is associated with a hexagonal C ring in the LiC₆ structure. To date, much research effort has been focused on the chemical processing and electrochemical properties of lithium-intercalated graphite. Aurbach and Ein-Eli¹² used diffuse reflectance Fourier transform infrared spectroscopy (FTIR) to show that the performance of electrodes containing Li-intercalated carbon in rechargeable batteries is strongly

dependent on the surface chemistry of the carbon. Recently, they investigated the behavior of graphite electrodes in various electrolyte solutions by using *in situ* XRD.¹³ These results suggest that the structural properties of the carbonaceous material are important parameters that influence the voltage profile, reversibility, and the final stoichiometry of the lithium-intercalated carbon. However there is still a lack of direct experimental evidence to relate structural information to the properties of lithium-intercalated carbons. In this work we report on the use of HRTEM to examine the microstructures of graphite that is intercalated with lithium. The results from electron microscopy are compared to data obtained by XRD.

Experimental

The graphite SFG6 from Lonza G + T Ltd was investigated. This is a highly anisotropic synthetic graphite that has been heat-treated at temperatures up to 3000°C before it is ground and fractionated to small particles with an average particle size of 6 μ m. The graphite powder was used directly to fabricate electrodes according to a procedure described earlier.¹ The graphite electrodes were lithiated by physical contact to a piece of lithium foil to short circuit the electrode at near 0 V. The two pieces were pressed and immersed in 0.5 M lithium trifluoromethanesulfonimide, LiN(CF₃SO₂)₂ (trade name HQ115, 3M Corp.) in 50/50 ethylene carbonate (EC)/dimethylcarbonate (DMC) (Grant Chemical) for at least 3 days. The fully lithiated SFG6 graphite has a golden luster, indicative of a stage-one compound. Subsequent electrochemical experiments with the lithiated graphite samples showed the characteristic flat voltage profile and deintercalation capacities close to 370 mAh/g (LiC₆). We have also examined graphite samples that were intercalated with lithium in an electrochemical cell after completing two intercalation/deintercalation cycles.¹⁴ Samples obtained from either intercalation procedures showed similar (dein-

* Electrochemical Society Active Member.

tercalation) capacity and voltage profiles. The electrochemical performance of SFG6 electrodes has been discussed elsewhere.¹

Specimens examined by HRTEM were prepared by the following procedure. The lithiated carbon samples were rinsed three times in a fresh (50:50) EC/DMC solvent for about 15 min. The samples were then dried at room temperature under vacuum for 0.5 h. The dried lithiated SFG6 electrodes continued to exhibit the golden appearance indicating the presence of intercalated lithium. The samples were ground to fine powders using a mortar and pestle inside an argon-filled glove box (<15 ppm H₂O). The finely divided powder was dispersed on a holey carbon film (TEM specimen holder), and then the specimen was sealed in argon-filled vials with a thin layer of wax (Parawax, Bromar, Inc.) for storage and transport to the TEM. The specimens were then quickly inserted into the chamber of the TEM. Despite precautions taken to avoid exposure to air, the specimen was briefly exposed for approximately 1 min during transfer into the microscope.

The dried lithiated electrode samples were encapsulated for XRD analysis. Small pieces of the sample (4 × 2 mm) were placed inside an argon-filled ampul that was obtained from a 2 cm section of 0.5 cm diam polyethylene shrink tube. They were then stored inside an argon-filled vial with a wax seal for transport. The encapsulated samples were introduced directly into the x-ray diffractometer. The samples were stable in these ampuls for several hours in air without any noticeable change in color.

The HRTEM facilities available at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory were utilized in this study. HRTEM using a Topcon-002B operated at 200 kV was used to analyze the crystallographic structure and particle morphology of the initial graphite and lithium-intercalated graphite. Conventional techniques were applied in the TEM studies of the samples. The XRD analyses were performed using a diffractometer (Siemens Diffractometer OSP, Model:D500, Germany).

Results and Discussion

Figure 1 shows the XRD patterns of SFG6 graphite with lithium intercalation, which has a distinct golden color. The intensity of the (002) diffraction peak at 1.85 Å ($2\theta \sim 48^\circ$) is higher than that of the (001) diffraction peak at 3.7 Å ($2\theta \sim 24^\circ$). This is consistent with the presence of lithium intercalated between the layer planes, with the dominant compound LiC₆.¹⁵ In addition to the LiC₆ and LiC₁₂ phases in the XRD results, there are some minor diffraction peaks which may be attributed to lithium hydroxide, LiC₁₆, LiC₄₀, etc. The disappearance of the diffraction peaks for graphite ($2\theta \sim 26^\circ$) in the XRD spectrum indicate that the graphite has been completely converted to lithiated graphite in our experiments.

A TEM photograph of the graphite used in the lithiation studies is presented in Fig. 2a. The highly ordered structure with well-defined layer planes which provides for facile Li intercalation is clearly evident. A d(002) spacing of 3.35 Å was determined by XRD. The TEM and selected-area electron diffraction (SAED) micrographs of lithiated graphite in Fig. 2b provide visual and structural information. The insets in Fig. 2b show the SAED pattern (right) and the morphology of LiC₆ (left) taken at low magnification. The [001] direction in the SAED gives a hexagonal pattern which is similar to that reported by Kambe *et al.*,⁹ and can be described by the α - β - γ interlayer stacking order. This hexagonal pattern is associated with grain b which has [001] out of the plane of the

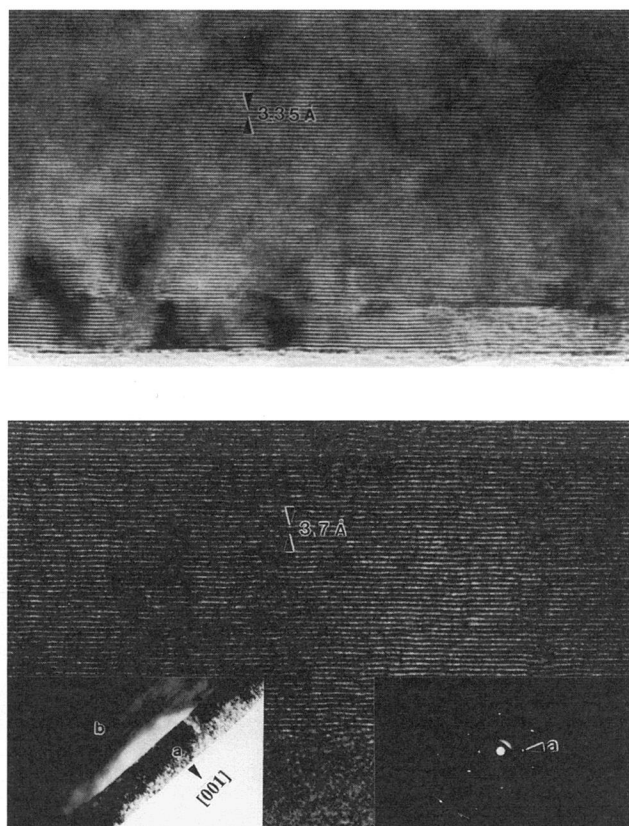


Fig. 2. High resolution TEM photographs of graphite (a, top) and the (001) layers in LiC₆ (b, bottom). The insets show the SAED pattern and the morphology of the particles taken at low magnification.

micrograph. In addition to the hexagonal pattern, we can see extra diffraction spots in the SAED pattern (grain a) designated by a. Kambe *et al.*,⁹ suggested the presence of superlattice spots in the SAED pattern but no detailed structural information such as lattice arrangement and real space morphology corresponding to the diffraction pattern were presented. The morphology of the area in the inset of Fig. 2b presents two grains with different orientations in the TEM photograph. The surface region of the lithiated graphite particle appears to be stick-like with a size near 1000 Å in width. The LiC₆ lattice image of the (001) layers with 3.7 Å spacing was arranged as nearly straight and regular layers as shown in Fig. 2b. The lattice image of the layers can be observed along the [100] or [010] direction of the particle, however the lattice images along the [001] direction cannot be observed with the TEM. Thus, the micrographs in Fig. 2b show that the crystal orientation of this stick-like grain is perpendicular to the interior of the grain with the hexagonal diffraction pattern. Close examination of the lattice image shows the presence of some defects in the lattice of the (001) layers in LiC₆ which appear to be associated with intermittent short-range disorder. The TEM image of the stage-two compound (not shown), LiC₁₂, appears similar to that of the stage-one compound except that the layer spacings are different. Examples of TEM observations of stage-one and stage-two compounds obtained from phosphorus-doped carbon were presented elsewhere.¹⁴

The XRD analysis showed that the layer spacing is 3.7 Å, consistent with LiC₆ formation. However, the superlattice from the intercalated lithium layers was not evident in the micrograph. Preliminary data indicate that the lithiated samples are unstable under the high-voltage electron beam in the vacuum of the TEM. It is believed that localized heating induced by the electron beam leads to loss of Li when the LiC₆ specimen is observed by TEM. SAED analyses showed changing diffraction patterns within several minutes of exposure to the electron beam. Efforts to understand this phenomena and improve the techniques for obtaining the superlattice associated with the lithium layer are in progress.

Recently, Oh *et al.*¹⁶ observed by XRD that LiC₆ changed to a mixed stage 1 and 2 of compound after contact with O₂/N₂ for 1 h. This result suggests that the specimens used in the TEM observations should not change noticeably during the short period they

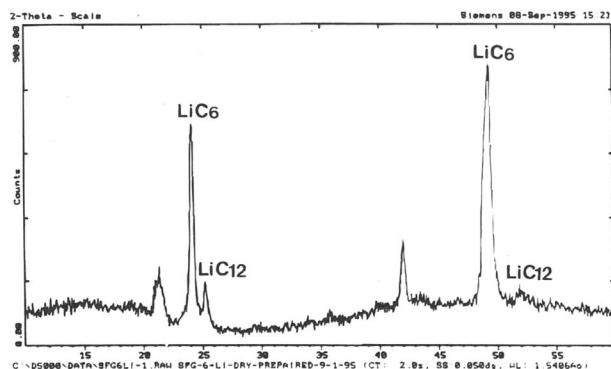


Fig. 1. XRD result of the lithiated graphite with distinct yellow color.

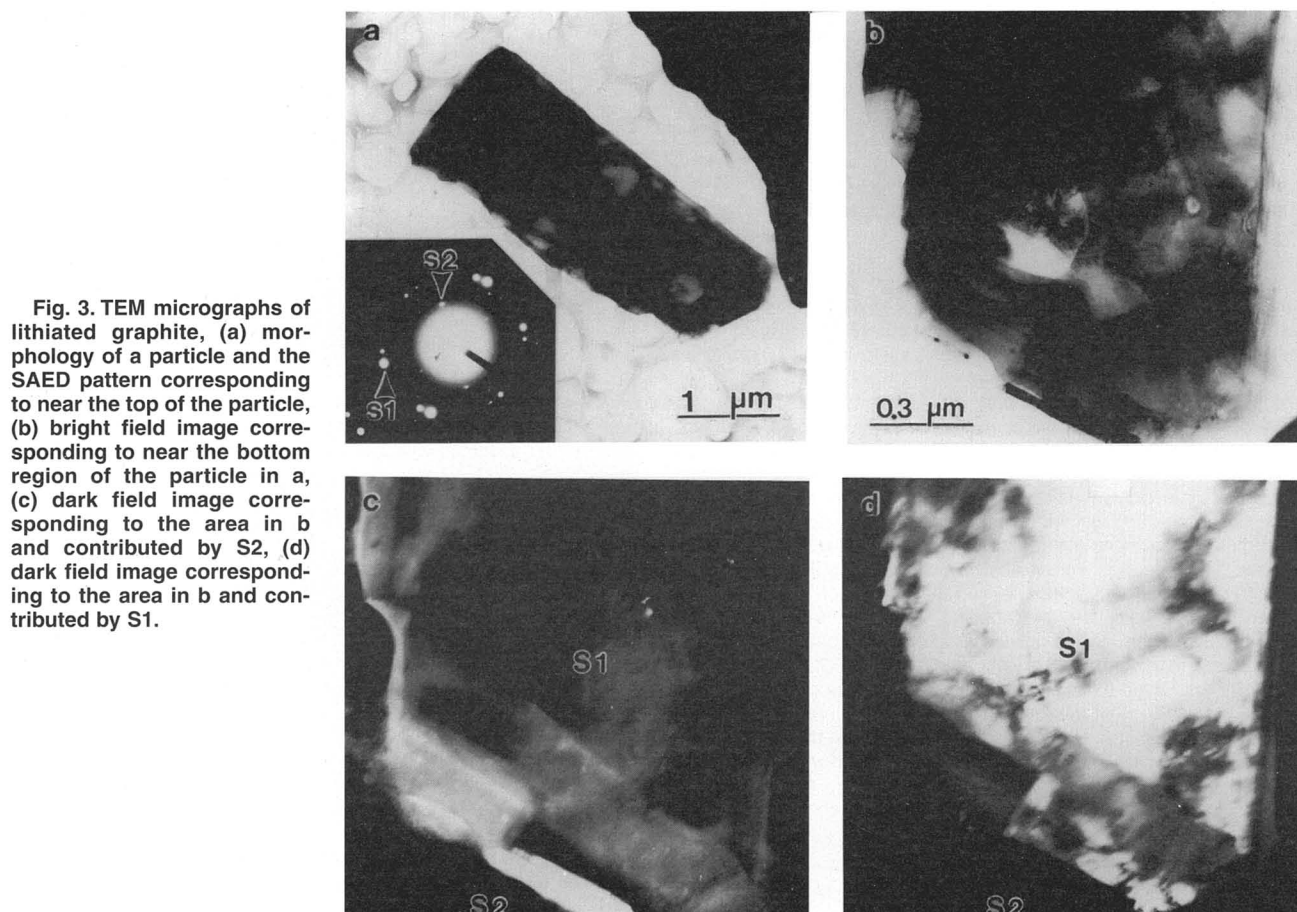


Fig. 3. TEM micrographs of lithiated graphite, (a) morphology of a particle and the SAED pattern corresponding to near the top of the particle, (b) bright field image corresponding to near the bottom region of the particle in a, (c) dark field image corresponding to the area in b and contributed by S2, (d) dark field image corresponding to the area in b and contributed by S1.

were exposed to air. To examine the presence of LiC_6 and LiC_{12} in lithiated graphite, the dark field (DF) technique of TEM was used. Figure 3 shows a set of TEM micrographs of a lithiated SFG6 graphite particle. The morphology of a typical lithiated graphite particle ($3.5 \times 1.3 \mu\text{m}$) is shown in Fig. 3a. The inset in Fig. 3a is a SAED pattern taken from this particle, and it indicates that the particle is composed of at least two structural phases. The photographs of higher magnification in Fig. 3b, which show areas with different contrast in the particle, indicate there are two or more regions with different phases or orientations, in agreement with the SAED results. The SAED pattern in Fig. 3a is attributed to a contribution by LiC_6 (marked by S1) and LiC_{12} (marked by S2). To examine the distribution and morphologies of these different phases, the DF images were taken that correspond to the bright field (BF) image in Fig. 3b using the diffraction spots in Fig. 3a. Figure 3d is a DF image contributed by diffraction spots from the hexagonal pattern in Fig. 3a, and shows a large area of dark contrast marked by S1 in the particle. Figure 3c shows the DF image contributed by diffraction spot S2 (LiC_{12}); the contrast of S1 has changed to white and the S2 (LiC_{12}) area has changed from white (in Fig. 3d) to dark. From an analysis of the BF and DF images, it appears that the LiC_{12} phase is located near the surface of the particle as shown in Fig. 3c, and LiC_6 is the dominant phase in the particle, as noted in Fig. 3d. Thus, the TEM micrographs of a lithiated graphite particle in Fig. 3 illustrate the morphology and distribution of the LiC_6 and LiC_{12} phases. The TEM results described here provide visual information on the microstructural properties of lithiated graphite. However, a detailed understanding of lithium storage in amorphous carbons is not available. This is the subject of ongoing work in our laboratory.

Conclusion

The lattice image with a spacing of $3.7 \text{ \AA}$ for LiC_6 was directly observed by HRTEM. The morphology and distribution of the LiC_6 and LiC_{12} phases were also observed by DF and SAED. The results indicate that LiC_6 and LiC_{12} can coexist in the lithiated graphite particle, and the surface of the particle can have a different Li concentration than the bulk.

Acknowledgment

The authors are grateful to the National Center for Electron Microscopy for use of the TEM facilities and thank F. Ross, C. Nelson, C. Echer, J. Turner, and D. Ah Tye for their assistance and helpful discussions. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric & Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Manuscript received Feb. 5, 1996.

Lawrence Berkeley National Laboratory assisted in meeting the publication costs of this article.

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Natural Organics and Environmental Stability of Mercury

Electrochemical Considerations

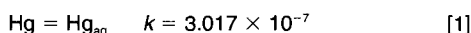
Desmond Tromans,^{*,a} John A. Meech,^b and Marcello M. Veiga^{b,c}^aDepartment of Metals and Materials Engineering, ^bDepartment of Mining and Mineral Processing, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

ABSTRACT

The behavior of elemental mercury in aqueous systems containing organics has been examined thermodynamically in terms of the complexing effect of a natural organic ligand species on aqueous electrochemical equilibria in the Hg-H₂O system, and supplemented by tests on liquid mercury exposed to solutions containing natural organics. The implications of the study are serious in relation to the likely effect of organic-containing aquatic systems on mercury solubility in the mercury contaminated regions of the world.

Introduction

Mercury is an extremely toxic element and contamination of natural waters may lead to mercury poisoning. The maximum solubility of the aqueous unoxidized mercury species in water, Hg_{aq}, is determined by the equilibrium reaction between Hg_{aq} and the liquid metal, Hg, according to Eq. 1



where k is the equilibrium constant obtained from the chemical free-energy data compiled by Balej¹ and edited by Bard *et al.*,² as listed in Table I. Consequently, the equilibrium activity of [Hg_{aq}] at 25°C is 3.017×10^{-7} , corresponding to a Hg_{aq} solubility of 6.05×10^{-2} ppm (parts per million by weight).

There are regions in the world where early mining practices used elemental mercury for the extraction of fine placer gold

* Electrochemical Society Active Member.

^c Present address: Metals Research Corporation of America, Vancouver, British Columbia, Canada.

Table I. Standard chemical free-energies (G°) at 25°C (Ref. 1, 2).^a

Species	State ^b	G° (kJ/mol)
Hg	l	0
Hg _{aq}	aq	37.2
Hg ⁺	aq	76.804
Hg ²⁺	aq	164.703
Hg(OH) ⁺	aq	-52.01
Hg(OH) ₂	aq	-274.5
HgO (red form)	s	-58.555
HHgO ₂ ⁻	aq	-190
HgCl ⁺	aq	-5
HgCl ₂	s	-180.3
HgCl ₂ ⁻	aq	-172.8
HgCl ₃ ⁻	aq	-308.8
HgCl ₄ ²⁻	aq	-446.4
HgCl	s	-105.187
Cl ⁻	aq	-131.056
H ₂ O	l	-237.178
H ⁺	aq	0
H ₂	g	0
O ₂	g	0

^a References 1, 2, use the symbol ΔG° for free-energies of species.^b aq = aqueous, s = solid, l = liquid, g = gas.

deposits by amalgamation techniques. The resulting Hg-Au amalgam was heated in a distillation retort or partially open pan and mercury removed by evaporation, leading to mercury accumulation in the surrounding area. A detailed review has been presented by Veiga.³ The amalgamation technique was used by gold miners in North America during the 1860s in Idaho and southern Oregon,⁴ and by Canadian miners along the benches of the Fraser river between Hope and Lillooet in British Columbia.⁵ Despite the known toxicity of mercury, amalgamation is still used extensively by informal mining operations (garimpos) in five major gold field areas in the Amazon region of Brazil.⁶ The garimpos play a major role in the regional economy and their crude distillation practices contribute to widespread mercury pollution.⁷ It is estimated that 4.5 million people are either directly or indirectly associated with Amazon mining operations,⁸ many of whom may be at risk from the mining-related contamination of the natural environment. For example, fish species are the main source of food for most Amazonian communities and mercury bioaccumulation in the Amazon was reported as early as 1984 by the Jacques Cousteau Society.⁸ Since 1984, medical tests have shown that people living within and distant from the garimpos have high levels of mercury in their blood⁹ and mercury contamination of the fish and people of the region has become widely recognized.^{6,10} Increased attention is now being given to determining those factors likely to increase the concentration of dissolved mercury in the aquatic systems of the Amazon region.

Oxidized forms of mercury are more soluble than the unoxidized Hg_{aq} species. Also, the oxidized form is more readily converted to the highly toxic methyl mercury, which accumulates in fish and enters the food chain.⁶ In this study we examine the possible effects of naturally occurring organic species on the stability and solubility of mercury in the natural aquatic environment.

Oxidation of Hg-Aqueous Equilibria

In the absence of organics.—Oxidation of Hg in aqueous systems is governed by the solution pH and electrochemical potential (E) imposed on the metal as a result of oxidizing species in the environment, of which dissolved oxygen is the most common oxidant in natural waters. The aqueous electrochemical equilibria determining the behavior of Hg are most conveniently represented in the form of E -pH diagrams of the type pioneered by Pourbaix,¹¹ based on the standard chemical free-energies (G°) of all the species involved. A list of species considered here, together with their G° values at 25°C,^{1,2} is presented in Table I.

With respect to Table I, the aqueous ion of the Hg^I oxidation state is represented simply as Hg⁺, although it is generally considered to exist in solution as the diatomic species Hg₂²⁺. The Hg⁺ designation is used as a convenience for calculation, with the recognition that $G_{\text{Hg}_2^{2+}}^\circ = 2G_{\text{Hg}^+}^\circ$. This allows an activity-independent boundary line to be plotted on the E -pH diagram where the activities of soluble Hg^I and Hg^{II} species (e.g., [Hg⁺] and [Hg²⁺]) are