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Comments

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Comment on graphite intercalated with H_2SO_4

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Salaneck, Brucker, Fischer, and Metrot [Phys. Rev. B $\underline{24}$, 5037 (1981)] have stated that x-ray-photoelectron spectroscopic data indicate that the intercalant of the graphite–sulfuric-acid system consists of species containing a variety of $S_nO_{4n}{}^{2-}$ ions. We question the evidence for these peroxy sulfate species, since $C_{17}{}^+$ can be formed at potentials 0.23 to 0.38 V below that necessary to make $S_2O_8{}^{2-}$. The reaction of the chemically similar SO_4F^- species with graphite yields a product which does not contain SO_4F^-, suggesting that strong chemical oxidants will not be stable with respect to graphite.

In a recent paper Salaneck, Brucker, Fischer, and Metrot[1] (SBFM) claim that a valid description for an intercalant layer in the "graphite–sulfuric-acid" system would consist of a hydrogen-bonded network of negative ions, including *both* $SO_4{}^{2-}$ and $S_2O_8{}^{2-}$, a proposal quite in contrast with the past formulation of $C_{24}{}^+$ $(HSO_4{}^-)$ $(H_2SO_4)_2$ for the first-stage compound.[2–4] The change in fractional ionization resulting from anodic oxidation from $C_{27}{}^+$ to $C_{18}{}^+$ was stated to correspond to loss of H^+ from the sample.[1] There was no explicit evidence for $S_2O_8{}^{2-}$ in the S 2*p* x-ray–photoelectron spectroscopy (XPS) core-level spectra, although much discussion arose from an excitation feature in the C 1*s* XPS core-level spectrum located at 16 eV versus the main 284.4-eV peak of highly oriented pyrolytic graphite (HOPG), which occurred in *both* an overoxidized $C_{12.6}{}^+$ compound and in H_2SO_4 *on* HOPG. While SBFM noted that their spectra were "not inconsistent" with the proposal of $S_2O_8{}^{2-}$ ions in the first-stage graphite–sulfuric-acid system, several lines of evidence argue against the proposal.

Besenhard has published galvanostatic data (i.e., potential versus charge passed) for the electrochemical intercalation of sulfuric acid into well-oriented pyrolytic graphite.[5] There are two voltage plateaus, one of 0.93 V [versus saturated calomel electrode (SCE)] beginning at $C_{48}{}^+$ and one of 1.46 V (versus SCE) beginning at $C_{21}{}^+$. The 1.46-V plateau extends from $C_{21}{}^+$ to $C_{17}{}^+$, which marked the termination of the experiment. The voltage necessary to generate $S_2O_8{}^{2-}$ from $SO_4{}^{2-}$ is 1.84 V [versus SCE, equal to 2.08 V versus normal hydrogen electrode (NHE) (Ref. 6)], which is 0.38 V *higher* than the potential of the chemistry in the $C_{21}{}^+ - C_{17}{}^+$ system. These numbers immediately suggest that $S_2O_8{}^{2-}$ could be used as a *chemical* oxidant to make $C_{24}{}^+$ $(HSO_4{}^-)(H_2SO_4)_2$, as was in fact demonstrated by Rüdorff in 1938.[7] Furthermore, one sees that graphite would be a poor electrode material for $S_2O_8{}^{2-}$ electrosynthesis, as was discovered by Matsuda in 1937.[8]

Strong oxidation of graphite, whether through high electrochemical potentials or through strong chemical oxidants, will result in covalent bonds.[9] A reaction which we have studied which has relevance to the $S_2O_8{}^{2-}$ proposal is the one between graphite and $CsSO_4F$,[10] which has a potential of about 2.5 V versus NHE.[11] Fluorine NMR of a product (SP-1 graphite-$CsSO_4F$ in HF, 10-wt.% gain, $d_{\max}$ x-ray-diffraction = 350 pm) shows possible evidence for SO_3F^- (3 ppm upfield from $CFCl_3$) and for HF (200–210 ppm upfield) but not for the initial SO_4F^- (132 ppm downfield). Similar results are found for the reaction of IF_7, XeF_6, or BF_3/ClF with graphite, with no evidence that the initial, strong, oxidant persists in the graphite following reaction.[12,13]

The role of H^+ in the graphite–sulfuric-acid system merits discussion. While there is no doubt that graphite-acid-salt systems exhibit hydrogen bonding,[14] it is not clear why such a system should exhibit two distinct hydrogen peaks in the proton NMR, as discussed by SBFM. Rapidly exchanging, liquidlike systems should give one peak in proton NMR, and we, in fact, find only a single peak in "H_2SO_4-intercalated graphite" made by the Rüdorff method with $K_2S_2O_8$ as a chemical oxidant (^1H at 35 MHz, 23 °C). Furthermore, if H^+ is being removed as H_2 from the graphite *anode* in the range $C_{27}{}^+$ to $C_{18}{}^+$, one notes that this is a chemical rather than an electrochemical oxidation of the compound since electrochemical hydrogen evolution would occur at the *cathode*. Finally, it is tempting to associate the 16-eV carbon spectral feature with a protonated graphitic "macrocarbonium ion," the analogous chemistry of which is known for small aromatic molecules.[15,16]

Note added in proof. Two recent papers on the electrochemistry of the graphite–sulfuric acid system have placed the potential of the second plateau at 1.61 V (versus SCE[17]) and 1.56 V (versus SCE, equal to 1.8 V versus NHE[18]). Thus, the highest voltage so far reported, 1.61 V, is 0.23 V lower than that necessary to make $S_2O_8^{2-}$. In the Nernst equation (298 K, $n = 2$), an endothermic voltage of 0.23 V corresponds to an equilibrium constant of $10^{-7.8}$. Metrot and Fischer[19] have shown that this second voltage plateau (which they measured as 1.70 to 1.75 V versus NHE) extends from C_{21}^{+} to C_{12}^{+}. SBFM have stated that the observed hydrogen gas evolves at the cathode; we point out that this observation does not necessarily require H^{+} to be concurrently lost at the anode (see, for example, Ref. 20).

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