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Reply to "Comment on graphite intercalated with H_2SO_4"

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We defend our proposal that peroxidation can account for most of the charge accumulated between $C_{27}{}^+$ and $C_{12}{}^+$ in the graphite-bisulfate intercalation system.

In the preceding Comment[1] Ebert and Appelbaum (EA) object to our proposal[2] (originally made in Ref. 3) that electrochemical overoxidation of graphite in pure H_2SO_4 might lead to partial conversion of bisulfate ions $HSO_4{}^-$ to $S_2O_8{}^{2-}$. Our proposal is not at odds with the usual formulation $C_{24}{}^+HSO_4{}^- \cdot 2H_2SO_4$ for the stage-1 compound since we postulate the peroxy species only when the graphite is charged beyond $C_{21}{}^+$. The main appeal of our hypothesis is its ability to account for a doubling of the charge per C atom with no change in the charge density on the carbon layers (hence the constant potential from $C_{21}{}^+$ to $C_{12}{}^+$—see Ref. 3).

X-ray photoelectron spectroscopy (XPS) data are cited[2] as being consistent with the proposal; the need for confirming molecular spectroscopy is made clear. The fact that the 16-eV C 1*s* feature occurs in "H_2SO_4 on HOPG" (highly oriented pyrolytic graphite) as well as in the overcharged $C_{12.6}{}^+$ compound is explained by noting that the former is actually a (spontaneous) intercalation compound[2]; HOPG is not an inert substrate for H_2SO_4 films.

EA concentrate their critique on an 0.4-eV inconsistency among several electrochemical results. The apparent discrepancy with Besenhard[4] results from different reference electrodes and overly literal interpretation of cell potentials in less-than-perfectly characterized electrochemical systems. Our potentials are relative to a counterelectrode which functions with hydrogen evolution, close to a normal hydrogen electrode (NHE). These potentials, determined in concentrated H_2SO_4, should only be compared *with extreme caution* to those of the usual redox scale determined in aqueous electrolytes. The electrode Hg_2Cl_2 [saturated calomel electrode (SCE)] used by Besenhard is unstable in H_2SO_4, requiring the use of scavenging salts which lead to uncertainties in the junction potential of up to several hundred meV. It is well known that persulfate leads spontaneously to $C_{24}{}^+$ (stage 1), but the *normal* potential ($P_H = 0$, molar concentration) of the system $S_2O_8{}^{2-}/SO_4{}^{2-}$ is 2.08 V relative to NHE, clearly greater than the stage-2–stage-1 plateau at 1.17 V versus NHE found by Besenhard. On the other hand, the difference of 0.38 V (noted by EA) between $S_2O_8{}^{2-}/SO_4{}^{2-}$ in water and the overoxidation potential 1.70 V versus NHE in H_2SO_4 may not be significant in light of the above-noted uncertainties.

The proposed oxidation of $HSO_4{}^-$ to $S_2O_8{}^{2-}$ takes place between carbon monolayers, thermodynamically quite unlike the usual aqueous conditions. The oxidation could even be enhanced by the proximity of the carbon macrocations and especially by an excess of free SO_3 which could produce the polymeric ion $S_4O_{14}{}^{2-}$. Recall that the $C_{12}{}^+$ was prepared in 10% oleum. Finally, the $C_{12}{}^+$ compound is a stronger oxidizer than $C_{24}{}^+$: It quickly oxidizes $M_n{}^{2+}$ to $M_n{}^{VII}$ in aqueous solvent, as does persulfate.

In summary, lacking any reasonable alternatives, the proposed oxidation of $HSO_4{}^-$ to $S_2O_8{}^{2-}$ (with H^+ reduced to H_2 at the cathode) explains the large increase in *apparent* charge per C atom, the lack of change in the free carrier plasma frequency,[3] and the fact that the crystal structure of the overoxidized $C_{12}{}^+$ compound is still lamellar rather than covalent. If *all* the accumulated charge were attributed to C–O or C–OH, the material would resemble Teflon more than an acid salt synthetic metal.

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[1] L. B. Ebert and E. H. Appelbaum, Phys. Rev. B 28, 1637 (1983), preceding Comment.

[2] W. R. Salaneck, C. F. Brucker, J. E. Fischer, and A. Metrot, Phys. Rev. B 24, 5037 (1981).

[3] A. Metrot and J. E. Fischer, Synth. Met. 3, 201 (1981).

[4] J. O. Besenhard, H. Mohlwald, and J. J. Nickl, Synth. Met. 3, 187 (1981).