



Letter to the Editors

I am writing in connection with the article published in *J. Power Sources*, Vol. 70 (1998) pp. 8–15 by Wen-Hong Kao of Johnson Controls.

In Table 1, Kao reports, without any collateral supporting data, that TiO_x “dissolves or decomposes in sulfuric acid”. Elsewhere, he further defines this criterion as “being the loss of more than 1% of weight, or changes in crystal structure to a non-conductive state” after being aged with PbO_2 and sulfuric acid for 7 to 9 days at 40 or 60°C.

As manufacturers of the Ebonex[®] range of materials which is often inaccurately and unscientifically referred to as TiO_x we were surprised to see this report which contradicted our own work and that of many of our customers and collaborators; and particularly in view of comments by Kao himself, with Patel and Haberichter (*J. Electrochem. Soc.*, Vol. 144, No. 6, June 1997) where it is stated (p. 1908) that “the half-life of this material in 4.5 M sulfuric acid at room temperature is estimated from the equation to be about 75.5 years...” and “based on these results Ebonex[®] (ceramic) is considered stable in the positive plate of a lead/acid battery”.

In the referenced paper, it appears that the sample of ‘ TiO_x ’ used in the experiment was manufactured in-house at Johnson Controls, and the exact stoichiometry was not reported. A patent case (see US Patent No. 5173215) teaches that the exact phase analysis of these materials rather than the overall stoichiometry is a key element of their corrosion resistance, and with this in mind Atraverda commissioned an external laboratory (London & Scandinavian Metallurgical) to repeat the corrosion experiment that Kao carried out. They used material nominally ‘ TiO_x ’ but of a well characterised phase assembly. In particular, care was taken to exclude from the samples tested any significant quantity of Ti_3O_5 , Ti_2O_3 and TiO , leaving only the Magneli series which are generally accepted to have the

stoichiometry $\text{Ti}_n\text{O}_{(2n-1)}$, starting with Ti_4O_7 (i.e., $n = 4$) and which exhibit corrosion resistant sheared rutile crystallography.

The figure established for the weight loss as a result of mixing with PbO_2 , leaching with sulfuric acid (SG 1.305) and thermostating for 7 days at 40°C (the method exactly as Kao reports) is 0.16%. There were no discernible changes in the phase assembly of the material (by XRD) before and after this treatment. We speculate that this disparity results from Kao’s sample containing quantities of the lower oxides and therefore being subject to significant corrosion.

We consider it important that this matter should be clarified in the context of Atraverda’s business where we are developing a bipolar lead/acid battery based on an Ebonex[®]/resin composite electrode material, exactly the application targeted by Kao. The material has been on test with several leading battery companies for a number of weeks now and one of them has noted that the corrosion current exhibited by the material is “30 times better than the next best”. None of them have discontinued testing on the basis of poor corrosion resistance of the Ebonex[®] material. Preliminary tests on paste adhesion have shown promise. Unlike the silicides of titanium, niobium and tantalum which Kao concludes are the best candidates in this role the Ebonex[®] material is available at reasonable cost and its success as an enabling technology for bipolar lead/acid batteries has the potential to revolutionise the industry.

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