

Electrochemical and Mössbauer studies of new iron-substituted γ -MnO₂ phases

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γ -MnO₂ is widely studied for its use in alkaline primary batteries. Among the numerous efforts made to improve their properties, various authors report the substitution of manganese for other transition metals (ref 1). Nevertheless, all the substitution ratios reported in the literature are less than four or five percent, and were never completely proved.

Using chemical synthesis, we managed to synthesize γ -MnO₂ powders containing 0% to 30% of iron as deduced from Energy Dispersion Spectroscopy studies. We then conducted numerous studies on these phases using techniques like Scanning Electron Microscopy, X-rays diffraction or thermal analysis. All the results are in favor of a manganese substitution for iron. For example, all samples present a single type of particles morphology that does not change with the iron amount. In the meantime, structural studies show that the presence of iron does not change the ramsdellite-type structure. Position and intensity of the reflections continuously vary but one cannot observe the appearance of any new reflection (Fig.1).

The different samples have been electrochemically reduced in 9M KOH versus platinum, and compared to pure γ -MnO₂ prepared in the same conditions. The reduction curve profile depends on the iron amount. While the first electron discharge is not drastically affected, the second one is (Fig.2). The length of the plateau at -0.4 volt vs Hg/HgO is reduced while the iron amount is increased, and there is appearance of a second plateau around -0.8 volt vs Hg/HgO. Surprisingly, the first plateau that is attributed to the reduction in solution of Mn³⁺ into Mn²⁺ (ref 2) has almost disappeared with only 20% iron in the sample. Note that the second plateau around -0.8 volt does not correspond to any known iron or manganese compound reduction.

Therefore, in order to undoubtedly prove the substitution and explain the overall reduction process, we conducted Mössbauer spectroscopy measurements both on the starting samples and during the reduction of the one containing 20% iron (Fig.3). The evolution of the Mössbauer spectra with the iron amount corresponds to a statistical distribution of the iron atoms in octahedral environment as expected in the case of a substitution. During reduction, Mössbauer spectroscopy throws some light on the involved mechanism.

References :

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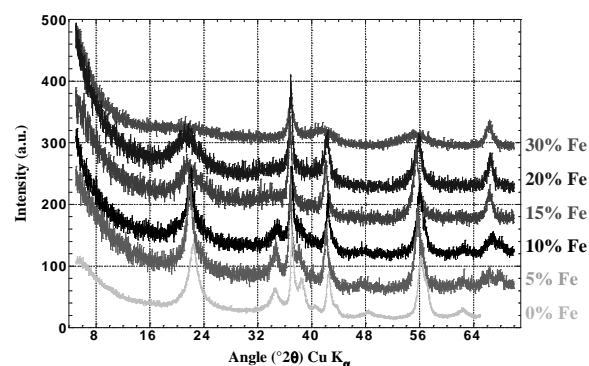


Fig.1 : X-rays diffraction patterns of the iron substituted γ -MnO₂ phases

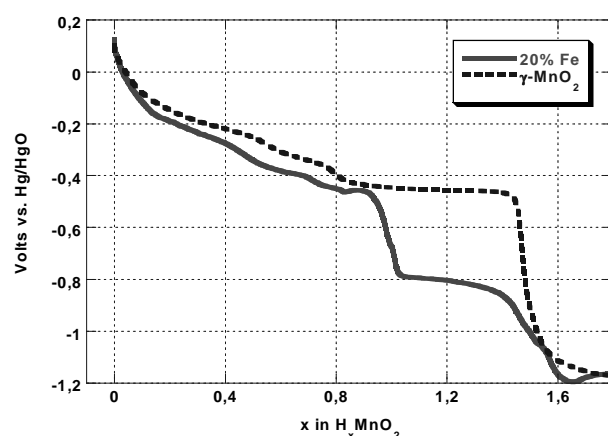


Fig.2 : Electrochemical curves of the reduction of γ -MnO₂ and 20% iron substituted γ -MnO₂ in 9M KOH

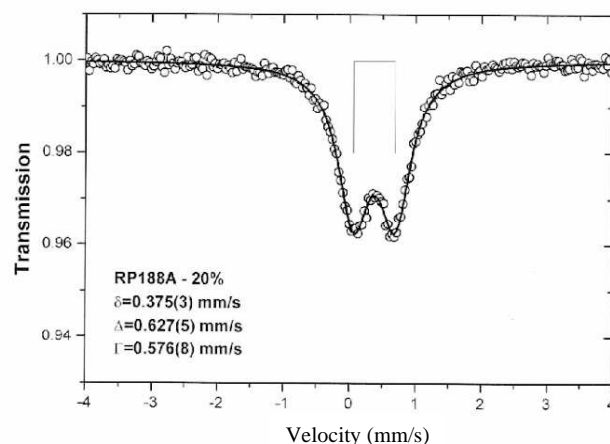


Fig.3 : Mössbauer spectrum of the 20% iron substituted γ -MnO₂