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Microstructure and Electrochemical Behaviour of Mg or Sr Doped Ilmenite ($FeTiO_3$) For Artificial Photosynthesis

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Extended Abstract

With the aim of displacing the conduction band of mineral ilmenite ($FeTiO_3$), and thus, enhancing its performance towards reductive reactions for artificial photosynthesis, samples of ilmenite were doped with either Mg or Sr by High Energy Ball Milling [1]. Analyses of the X-ray Diffraction patterns were carried out for all the obtained samples. Furthermore, the electrochemical behaviour of the samples was studied to establish the effects of the solvent, type and amount of binder in the preparation of the electrodes, as well as the effect of the insertion of Mg or Sr on the conduction band of the material.

XRD analyses evidenced that the microstructure of the samples was affected by the milling process, which led to the amorphization of the crystalline structure of ilmenite. Calculations of the lattice parameter and volume of the cell, carried out following Bragg's law and using the exact position of the characteristic peaks of the experimental patterns, showed that no significant changes were induced by the insertion of Mg nor Sr. These results can be attributed to the small amount of doping metal added to the process, and to the significantly heterogeneous nature of the samples, which hinders a profound analysis by XRD.

During the preparation of semiconducting electrodes based on doped ilmenite, ethanol and isopropanol were used as solvents, while nafion and α-terpineol were compared as binders. The electrochemical behaviour of the samples in redox reactions, analyzed by cyclic voltammetry, exhibited a high dependence of the current density on the solvent and the binder, proving that electrodes prepared with the mixture of α-terpineol and isopropanol exhibited a higher current density. In addition, the characteristic reduction reaction of the system was carried out at smaller potentials when using α-terpineol, thus suggesting a lower energy requirement for photo-reduction using this binder as compared to nafion. Furthermore, the electrodes prepared with α-terpineol showed smaller resistance to mass transfer compared to those prepared with nafion.

The electrochemical behaviour of the samples doped with either Mg or Sr was compared by cyclic voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS) through the analysis of the Nyquist diagrams and the Mott-Schottky plots. The results showed that the doping of the samples did not influence the mass transfer resistance of the material. On the other hand, the insertion of both Mg and Sr led to an increased concentration of electron donors which, at the same time, enhances electric conductivity and favours the mobility of charge carriers. As a consequence of the doping, the conduction band of the samples was displaced to more negative values, as it was expected. Finally, the samples doped with Mg exhibited a more stable electrochemical response compared to those doped with Sr, especially when using MgO as precursor; this can be attributed to an increased affinity of Mg with $FeTiO_3$.

References

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