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Electronic structure calculations for Pt-Sn intermetallic phases

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Abstract – First principles calculations in the study of periodic materials like the intermetallic phases have been played an important role in the characterization of the lattice geometry and the electronic structure of these materials. This work presents a study of the intermetallic phases $PtSn_2$, PtSn and Pt_3Sn which are considered representative materials in the investigation of electrocatalytic processes. The results show that the methodology applied here is well-suited for geometric and electronic properties calculations providing minimal errors for the lattice parameter optimization and predicting the PtSn phase as the best electrocatalyst material.

Platinum Intermetallic phases have been presented as promising materials in the development of the electrocalysis of fuel cell related reactions [1, 2]. In this way, it is imperative the characterization of the geometric and electronic structure of such materials and the first principles calculations are considered as an important tool for this purpose. In this work it is presented the investigation of $PtSn_2$, PtSn and Pt_3Sn intermetallic phases through *ab initio* methods by means of the Density Functional Theory (DFT) and using the PWscf (Plane-Wave Self-Consistent Field) package, as part of Quantum-ESPRESSO [3] distribution.

All calculations were carried out via Generalized Gradient Approximation (GGA) with the Perdew-Wang [4] electronic exchange-correlation functional. It was used Vanderbilt ultrasoft pseudopotential, a Monkhorst-Pack grid of 4x4x4 and an energy cutoff of 30 Ry for the wave functions. It was performed a geometric optimization of the intermetallic phases structures and the optimized parameters were employed in the electronic structure calculations, generating density of states (DOS) diagrams.

The lattice parameters obtained by the optimization procedure were compared to the experimental data and no significant variation was found among the data with errors lower than 2%. Figure 1 illustrates the projected DOS onto *d*-orbital for the Platinum, these orbital are the main contributor in the total DOS of the system and characterize the Pt sites as the actives sites for adsorption of molecules. In Figure 2 are represented the *d*-band center energies and its dependency of the platinum composition with the 1:1 phase showing an electronic structure distinguished. The *d*-band center theoretical parameter is crucial in the study of electrocatalysis since it determines the susceptibility of the material to promote the electron transference. A similar behavior was found in an experimental kinetic study performed in our laboratory that compares the electrochemical performance of these materials, with the PtSn phase presenting the best result and pointing to a good adsorption characteristic [5].

One can conclude that the methodology applied in this study allows us to attain important fundamental parameters for the electrocalysis as the geometrical and electronic structure of the materials that are preponderant to establish interaction in the adsorption processes.

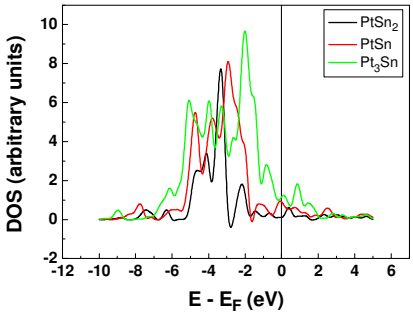

Figure 1: Projected density of states onto Pt *d*-orbital.

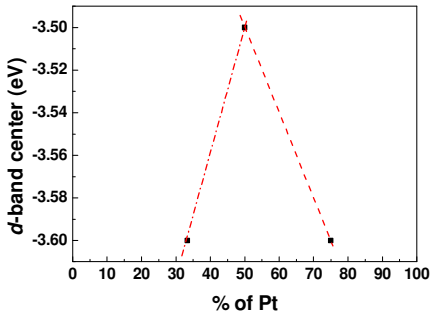

Figure 2: The *d*-band center energy as a dependency of the Pt composition.

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References

[1] E. Casado-Rivera, D.J. Volpe, L. Alden, C. Lind, C. Downie, T. Vazquez-Alvarez, A.C.D. Ângelo, F.J. Disalvo, H.D. Abruña Journal of the American Chemical Society, 126 (2004) 4043-4049.
[2] A.F. Innocente, A.C.D. Ângelo, Journal of Power Sources, 162 (2006) 151-159.
[3] S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari and A. Kokalj. <http://www.pwscf.org/>.
[4] J. P. Perdew and Y. Wang, Physical Review B, 45 (1992) 13244-13249.
[5] L.M.C. Pinto, A.F. Innocente, A.C.D. Ângelo, unpublished results, 2009.