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Constraints for the interpretation of XPS spectra of non-PGM TM-N_x (TM=Fe, Co; x=1,4) ORR electrocatalysts from first-principles simulations

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Fuel Cells are promising candidates for the energy conversion technologies in particular for non-stationary applications. A material set that continues to attract significant attention are non-PGM electrocatalysts with carbon embedded TM-N_x defects. XPS observations of the electrocatalyst after pyrolysis support the presence of various TM-N_x (TM=Fe, Co, x=1-4) defect moieties (See Fig 1).[1] However, the correlation between features in the XPS spectra and particular defect geometries and chemistries remains challenging and generally relies on the availability of suitable reference materials. In the absence of these reference materials the interpretation of nitrogen speciation based on N1s core-level-shifts (CLS) is more tentative.

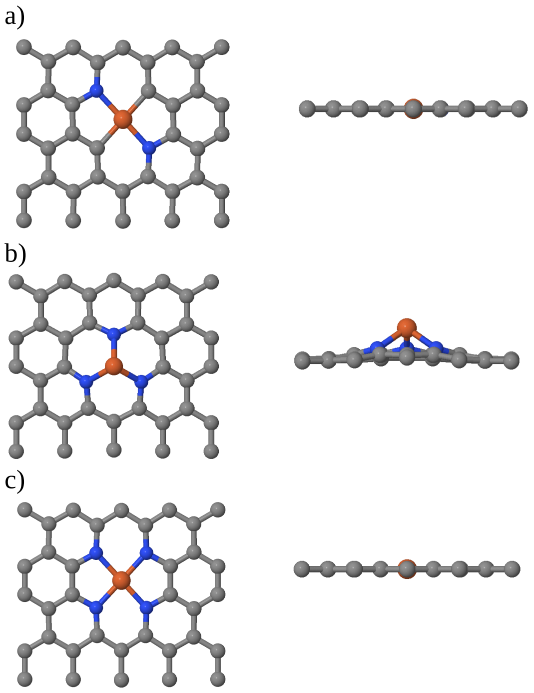

Figure 1 : Top and sideview of relaxed a) TM-N_2 b) TM-N_3 c) TM-N_4 defect in bilayer graphene. Grey = carbon; Blue = nitrogen; Red = Co, Fe.

Therefore it is desirable to provide independent estimates of CLS for assumed defects (Fig. 1). First-principles computations can provide this missing link by predicting core-level shifts for candidate chemistries and geometries of the catalytic sites.

The incentive of this research resides in the understanding of the electrochemical performance and energetics of these TM-N_x catalysts and the quest for the design of suitable catalysts with improved performance. Modern Density Functional Theory (DFT) computations can be used to calculate CLS for candidate geometries and chemistries. The computed XPS CLS can constrain XPS observations (Fig. 2) especially in cases where suitable reference structures are not available. All CLS are computed in the final state approximation at the PAW-GGA level. In particular we will discuss the geometry and chemistry dependence of N1s, Fe2p, and C1s CLS and compare different computational protocols where possible to experimental observations.[2]

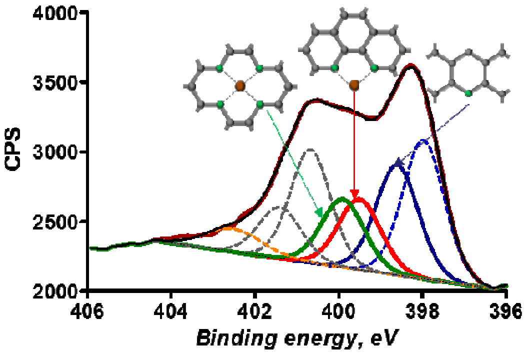

Fig.2: N 1s high resolution spectra of Aminoantipyrine–Fe catalysts.[2]

For both the reference system and the material of interest, binding energies (BE) for the same orbital are computed in the final state approximation and referenced to the Fermi-energy. Finally, CLS are computed as the difference of these two values.

This strategy allows to reduce or eliminate the effect of the steep near-nucleus coulomb potential on the BE shifts. Preliminary calculations where all nitrogen 1s electrons are excited simultaneously and relaxation is neglected show that N1s CLS are likely insufficient to uniquely fingerprint defect geometries and chemistries in XPS spectra. For example, N1s CLS relative to N_2(g) are predicted to be 3.8 eV, 1.8 eV, 1.8 eV, and 2.3 eV for nitrogen-doped graphene, Fe-N_2, Fe-N_3, and Fe-N_4 defect motifs, respectively. This indicates that Fe-N_2 and Fe-N_3 may appear at a similar location in XPS spectra.

CLS can be affected in some cases by electronic/structural relaxation in the computations. The preliminary results were computed without taking relaxation into account. The significance of this additional parameter relies on the knowledge of the lifetimes of the excited states which at present remain unknown. We will discuss several computational protocols to compute CLS from first-principle simulations and the effect of relaxations in the final state.

The capability to predict BE shifts independently from first-principles theory for candidate geometries, allows us to establish structure/property relationships that are critical for the detailed interpretation of XPS spectra and the understanding of nitrogen speciation in non-PGM electrocatalysts.

References:

1. S. Kattel, P. Atanasov, B. Kiefer, *J. Phys. Chem. C*, **116**, 8161 (2012).
2. K. Artyushkova, B. Kiefer, B. Halevi, A. Knop-Gericke, R. Schlogl, P. Atanassov, *P. Chem Commun*, **49**, 2539 (2013).