Modelling electrochemical reactions: concepts, methods and challenges

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The presentation consists of two parts; the first part deals with the robustness of theoretical concepts used to assess activities of electrochemical reactions. The discussion will start from the oxygen reduction reaction (ORR) and from there it will be extended to other electrochemical reactions of interest. From the viewpoint of many computational electrochemists, there is an optimum binding energy for the ORR designated by volcano maximum, beyond which the activity is no longer controlled by oxygenated species coverage, but the inability to make OOH species. On the other hand, experimental electrochemists attribute activity decrease to the build-up of spectator species and therefore acknowledge only the strong (left) binding side of the ORR volcano. A special attention will be devoted in trying to elucidate this point of contention using on a somewhat different computational approach.

The second part deals with the current methodology for modelling strongly correlated oxides. A known artifact of Density Functional Theory is a self-interaction error, which tends to delocalize electron density. This effect particularly comes into play in transition metal (TM) compounds whose electronic structure contains many local features. The usual approach to deal with this problem is to apply the on-site Hubbard U correction to the localized (mostly d and f) states that participate in chemical bonding or to use hybrid calculations. We demonstrate on the example of perovskite oxides that formation energies and reaction overpotentials for the oxygen evolution reaction (OER) change by as much as 1 eV/V when changing the U (in DFT+U) and α (in HSE) values within the $0 - 5$ eV and $0 - 0.35$ range, respectively. We tackle the sensitivity problem by introducing a simple method, which allows for the calculation of bulk and surface energetics independent of the empirical parameters, and furthermore gives consistent results for the formation energies of oxygen vacancies in contrast to large errors bars observed in experiments. The method is benchmarked on the OER, but can be used in all other reactions, electrochemical or chemical, and processes (e.g. oxygen vacancy or Li-ion diffusion) which necessitate the use of TM compounds.