Electronic descriptor to identify the activity of SACs for e-NRR and effect of BF_3 as electrolyte ion

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Abstract: Electrochemical nitrogen reduction reaction (e-NRR) is an eco-friendly alternative approach to generate ammonia under ambient conditions, with very low power supply. But, developing of an efficient catalyst by suppressing parallel hydrogen evolution reaction as well as avoiding the catalysts poisoning either by hydrogen or electrolyte ion is an open question. So, understanding a class of catalysts in terms of its electronic properties and then correlate with their catalytic activity is a primary step to discover a correct catalyst in short span of time. In order to screen the single atom catalysts (SACs) for the e-NRR, we proposed a descriptor-based approach using density functional theory (DFT) based calculations. We investigated total 24 different SACs of types TM-Pc, TM-N_3C_1, TM-N_2C_2, TM-NC_3 and TM-N_4, considering transition metal (TM) from 3d and 4d group of periodic Table. We have considered mainly BF_3 ion to understand the role of electrolyte and extended the study for four more electrolyte ions, Cl, ClO_4, SO_4, OH. Herein, to predict catalytic activity for a given catalyst we have tested 16 different electronic parameters. Out of those, electronic parameter $d_{xz}\downarrow$ occupancy, identified as electronic descriptor, is showing an excellent linear correlation with catalytic activity (R^2 = 0.86). Furthermore, the selectivity of e-NRR over HER is defined by using an energy parameter ΔG_{*H}-ΔG_{*NNH}. Further, the electronic descriptor ($d_{xz}\downarrow$ occupancy) can be used to predict promising catalysts for e-NRR, thus reducing the efforts on designing future single atom catalysts (SACs).

[**Keywords:** Adsorption, Electrocatalyst, Descriptor, Ammonia, Electrolyte, SACs, DFT]