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Title:	RATIONAL DESIGN OF DIFFERENT COMPONENTS AND INVESTIGATION OF CORE PARAMETERS FOR ELECTROCATALYTIC REDUCTION OF DINITROGEN TO AMMONIA.
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Abstract:	<p>The over-consumption of the non-renewable energy sources tend the world-wide research to incline towards development of sustainable approaches to withstand the global energy demand. In this scenario, green hydrogen/green ammonia serve as a safe and reliable alternative towards an electrified future. Although to meet the practical demands of ammonia, the century-old Haber Bosch process is the sole option, but it deviates from the goal to a carbon neutral society. The electrochemical ammonia synthesis from dinitrogen reduction reaction (NRR) has been an emerging hotspot in the academia as well as industries owing to the ever-growing demands of green ammonia in fertilizer and transportation sectors. With a pledge of the "Net-Zero" society, different nations have been setting up ammonia plants with a target of few million tons of ammonia production in the coming two-three years. Realizing the gravity of the matter, it is extremely crucial to develop NRR electrolyzers capable of producing industrial scale ammonia, that too in an energy-efficient manner. However, with the conventional electrocatalyst-electrolyte systems it can only attain a 'niche' status in terms of commercialization. Thus, a rapid improvisation in the cell components is utmost required realising the key factors that manoeuvre the NRR kinetics, thermodynamics as well as energetics to achieve the desired goal. Before aiming high it is crucial to realize the rate limiting parameters of NRR that need to be worked upon to kinetically fasten the reaction kinetics, which is otherwise too difficult owing to the chemical inertness of N₂ and complicated multi-step reaction mechanism: (a) While the aqueous electrolytes provide ambient reaction conditions for NRR, but the poor N₂ solubility in such media limit the sufficient reactant access to the catalyst surface resulting into a low yield rate of NH₃. (b) Material selectivity poses a serious challenge on N₂ adsorption and make way for the more convenient hydrogen evolution reaction (HER) in the same voltage window. (c) The sluggish kinetics of oxygen evolution reaction (OER) retard the NRR process at the cost of high energy input and high overpotential, which disregard the prospects of this electrochemical approach. So, in this thesis works our major aim was to improve the yield rate and Faradaic efficiency (FE) of NH₃ synthesis and to realize the chemistry of active sites that intuitively manipulate the mechanisms and kinetics of the elementary steps of NRR. Primarily, we worked upon a new aqueous electrolyte NaBF₄ that could be handled ambiently, capable of forming N₂-BF₃ adduct that helped to bring a significant concentration of N₂ in the medium. Moreover, BF₃ helped to modulate the d-band center of Mn-N/C catalyst provoking N₂ adsorption and activation on the catalyst surface by a "push-pull" electronic effect. This multitudinous role of BF₃ resulted into 2.45 × 10⁻⁹ mol s⁻¹ cm⁻² production rate of ammonia, approaching the industrial scale periphery at 0.0 V vs RHE. Eventually we concentrated on adopting different strategies of catalyst synthesis, majorly keeping in mind few important factors like (a) to ensure better orbital overlap with N₂ improving the rate limiting potential, (b) N₂ adsorption over proton adsorption, (c) suppressed HER. The base material selectivity was such that either it should have inherent affinity towards N₂ or it should act as HER suppressant. Boron having orbital symmetry with N is expected to suppress HER. Thus, firstly we chose boron-carbonitride material and functionalized the edges with O-atom (BNCO). This induced a charging effect on B that consequently improved its binding tendency and charge transfer phenomenon with N₂. Realizing the importance of charge cloud density, we then focussed to engineer NPG@SnS₂ heterostructure material that caused a band-bending at the metal semiconductor interface to equilibrate the Fermi levels. A charge accumulation occurred on the SnS₂ side lowering the work function of the material with four-fold enhancement in conductivity. This strategy also deviated proton adsorption more favourably on the S atoms resulting into 49.3 % FE for NRR. Then we moved to Ag₃PO₄ since both the cationic and anionic parts are already proved to suppress HER. We intended to improve the active site density and thus we improvised the material with group-VIB metal doping. This doping assisted vacancy engineering strategy created additional dopant-Ag active sites and altered the electronic properties of the catalysts facilitating N₂ adsorption in a side-on manner via d- p orbital mixing, resulting in 54.8 % FE. But this vacancy engineering itself holds significant potential to impact the NRR performance of a material and thus to gain an in-depth understanding of this concept we developed oxygen-vacancy enriched SnO₂, where the bridge-type vacancy was found to be more electroactive and stable than the in-plane type vacancy. This enabled an end-on followed by side-on N₂ adsorption of the two Sn atoms adjacent to the bridge vacancy site. The proton adsorption being more favoured on the electronegative O-atom, HER got suppressed benefitting NRR with 48.5 % FE. A detailed kinetic and mechanistic investigations were carried out with rotating ring disc electrode (RRDE) technique and in-situ FTIR studies respectively together with theoretical support, that provide a wholesome survey of the impact of oxygen vacancy on the structural as well as electronic properties of the material that in turn affected the elementary steps of NRR. After attaining an appreciable NRR performance with several electrolyte-catalyst modifications, our intention deviated to a broader goal of improving the energy efficiency of this process. The several bottlenecks of NRR and on top of that the sluggish OER kinetics intakes about 90 % of the electricity input and raises the overall energy and power demand of the NRR process. So, we explored the inter-dependency of the NRR and OER processes and how the kinetics of one impacts the other. Upon replacing the conventional Pt counter electrode for OER, RuO₂ was found to not only improve the OER kinetics in 0.1 M KOH, but also enhanced the FE for NRR at a lower overpotential and current consumption. As a proof of concept, the FePc RuO₂ electrolyzer was constructed that displayed a high electricity-to-chemical energy conversion efficiency of 46.7%. The electrolyzer also forecasted a full cell voltage of 2.04 V, which demanded only 603 mV overpotential to attain 0.5 mA current to drive forward the chemical equilibrium of the overall NRR-coupled-OER process.</p>
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