ScienceDirect

iScience

Volume 25, Issue 10, 21 October 2022, 105179

Article

Regio-isomerism directed electrocatalysis for energy efficient zinc-air battery

Sanchayita Mukhopadhyay [1], Mruthyunjayachari Chattanahalli Devendrachari [1], Sandeep C. Kanade [1], Chathakudath Prabhakaran Vinod [2], Harish Makri Nimbegondi Kotresh [3], Musthafa Ottakam Thotiyl [1 4]

Show more

https://doi.org/10.1016/j.isci.2022.105179

Get rights and content

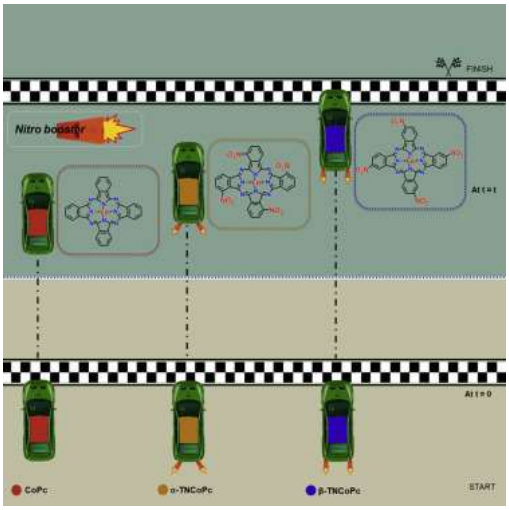
Highlights

- Ligand isomerism tunes the activity of the catalytic center
- Repulsive non-covalent interactions are responsible for the catalytic activation
- Ligand isomerism can improve the round-trip efficiency of a Zn-air battery

Summary

We have investigated the role of ligand isomerism in modulating the mechanisms and kinetics associated with charge/discharge chemistry of an aqueous metal-air battery. The dominant electron-withdrawing inductive effect (-I effect) and the diminished electron-withdrawing resonance effect (-R effect) in the α-NO_2 isomer noticeably diminishes the rate of oxygen reduction (ORR) and oxygen evolution reactions (OER) on the catalytic Co-center. In their β-counterpart, the cumulative –I and –R effects noticeably enhance the OER and ORR kinetics on the same catalytic Co-center. Therefore, the regioisomerism of the -NO_2 functionality amplifies the kinetics of ORR/OER without influencing their mechanistic pathways. When isomeric electrocatalysts are integrated to aid the charge chemistry of a Zn-air battery, the overpotential could be decreased by ~250mV with β-NO_2 isomer leading to a round-trip efficiency as high as 60%. This work contributes to the design of novel molecular platforms to target the overall round-trip efficiency of energy storage and conversion devices.

Graphical abstract



Download : Download high-res image (161KB)

Download : Download full-size image

Previous

Next

Subject areas

Chemistry; Electrochemistry; Electrochemical energy storage; Energy materials

Introduction

The ever-increasing demands for energy and awareness about climate change have made the transition from a fossil fuel-based energy economy to an alternative clean energy economy inevitable (Davidson, 2019) (Gao et al., 2021) (Ledendecker et al., 2015). This gradual process has been accelerated by recent research worldwide on sustainable energy harvesting, conversion, and storage (Chinnam et al., 2015) (Indra et al., 2018) (Liberman et al., 2020). In this context, various types of batteries have been developed with myriads of applications ranging from portable electronic devices, grid-scale energy storage to electric vehicles (Zhao et al., 2022) (Harper et al., 2019) (W. Li et al., 2019b) (Zhang et al., 2022) (Tabassum et al., 2019). Among these, metal-air battery technologies such as Zn-air batteries (ZABs) are projected as promising candidates for long driving range electric vehicles (EVs) mainly because of their high gravimetric energy densities in the range of 470W h kg^{-1}(Bruce et al., 2012) (Lee et al., 2011)(Jung et al., 2016) (Li et al., 2021). However, there are several challenges associated with aqueous rechargeable metal-air batteries. Firstly, it suffers from high charge/discharge overpotential due to the high overvoltage for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) which consequently leads to low round-trip efficiency typically in the range of ~50–60% (Liu et al., 2019) (Guo et al., 2018) (Liu et al., 2016). As far as ORR is concerned, the reaction is catalyzed by benchmark Pt-based noble metal electrocatalysts, which has several issues associated with cost and availability (Fu et al., 2017) (Peng et al., 2022). This necessitates exploration of durable electrocatalysts based on earth abundant non-noble metals. Secondly, ORR can proceed through variety of pathways and hence catalysts catalyzing the 4 electron ORR are often preferred for aqueous air batteries (Özen et al., 2016) (Xu et al., 2019). Besides, the higher charge voltage associated with OER often results in the degradation or corrosion of the air electrode, thereby, greatly reducing the cycle life of aqueous air batteries (Li et al., 2022) (Lee et al., 2014). Moreover, the benchmark OER electrocatalysts like IrO_2, RuO_2, etc., are low in abundance and consequently have high cost and are not very stable in strongly alkaline electrolytes which is often encountered in aqueous metal air batteries(Cherevko et al., 2016) (Ghareghashi and Mohebbi, 2020). In this context, the need of the hour is to develop alternative ORR/OER catalysts based on earth-abundant metals with high activity and durability for rechargeable ZABs (Özen et al., 2016) (Xu et al., 2019) (Bhowmick et al., 2020) (Anju et al., 2016).

Herein, we aim to explore ligand isomerism in molecular electrocatalysts like phthalocyanines for the ZAB discharge/charge reaction (ORR/OER) to target their overall round-trip efficiency. The choice of phthalocyanines is mainly based on the fact that these molecules are among the prime candidates that are being explored for various electrochemical applications because of their robustness, stability, and highly tuneable optoelectronic properties (Sobbi et al., 1993) (Bottari et al., 2010) (Complexes, 2007) (Sorokin, 2013). Among these phthalocyanines, we have explored the Co-based systems as they have been found to be electrocatalytically active toward ORR/OER (Kottaichamy et al., 2020)(Cong et al., 2005)(Fu et al., 2020) (C. Li et al., 2019a). Interestingly, when nitro-substituted cobalt phthalocyanines (TNCoPc) were explored for ZAB discharge/charge reaction, we found that the ligand isomerism (α and β-TNCoPc isomers) significantly tunes their respective kinetics without altering the mechanistic pathways of the reaction. The present work demonstrates an alternative approach in the design of efficient molecular electrocatalysts to target electrochemical reactions relevant to energy storage and conversion.