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Electrocatalysis for energy conversion reactions

Zhenyu Sun[ab]

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The continued consumption of fossil fuels and growing global energy demand are driving significant climate change and environmental degradation. Addressing these challenges urgently requires the advancement of clean and efficient energy technologies. One promising approach to achieving this goal lies in electrocatalysis, which facilitates chemical conversion by lowering the activation barriers of reactions and accelerating reaction kinetics (De Luna *et al.*[1]). Electrocatalytic reactions can use renewably generated electricity, enabling carbon mitigation and energy sustainability. Direct transformation *via* electrocatalysis can overcome the Carnot limit linked to traditional thermal processes that use heat. For these reasons, extensive efforts have been devoted to developing electrocatalysis for various emerging energy conversion processes, such as water splitting, fuel cell reactions, and carbon/nitrogen upgrading. The design and synthesis of high-performance electrocatalysts, catalyst evaluation, investigation of electrocatalytic mechanisms, and engineering of electrode/electrolyte interfaces, are the focus of much current research. These endeavours are expected to facilitate the development of electrocatalysts integrated with related industries toward a sustainable future. This themed collection on "Electrocatalysis for energy conversion reactions" aims to provide alternative ways to defossilize the energy industry and transform chemical energy into more usable forms. The following summarizes the findings of the publications in this themed issue.

To reduce anthropogenic carbon emissions and mitigate continued global warming, intensive work has been directed to capture CO_2 and convert the sustainable C_1 molecule into valuable chemicals and fuels. Direct electrochemical CO_2 reduction (ECR) provides an appealing route, due to operating at ambient conditions, harnessing renewable energy resources, and using water as a source of hydrogen without the need for H_2, favouring a net-zero-emission carbon economy (Sun[2]). ECR was first demonstrated by Hori *et al.* in the 1950s and has stimulated increasing research interest over the past decade owing to the rapidly decreasing cost of renewable electricity. A variety of metallic and metal-free electrocatalysts have been developed to improve conversion rate, energy efficiency, product selectivity, and electrolysis durability. Wijewardena and her colleagues (**https://doi.org/10.1039/D5SU00174A**) summarized recent advances in graphene-based materials as catalysts for ECR. Their work focused on strategies including heteroatom doping and metal–graphene hybridization to optimize catalytic performance. They discussed both conventional graphene-based materials and emerging graphene analogs for ECR.

Single atom catalysts (SACs) feature ultrahigh-atom utilization and a tailorable coordination structure, affording unique and high catalytic activity for many reactions. Al-Mahayni and coworkers (**https://doi.org/10.1039/D4SU00747F**) performed density functional theory (DFT) analysis to investigate four Ti- and Mo-based MXenes (Ti_2C, Ti_3C_2, Mo_2C, and Mo_3C_2) and ten supported single metal atoms (Ag, Au, Co, Cu, Fe, Ni, Ru, Pd, Pt, and Zn) for ECR to C_1 products (CO, HCOOH, CH_3OH, and CH_4). By calculating the formation energy of MXenes, binding energy of SACs, activity (H adsorption energy, reaction energy of the thermodynamic limiting step of CO_2 reduction reaction), and selectivity (the adsorption of CO_2 against the adsorption of H), five catalysts were screened to display good performance following the order $Ni@Ti_3$ > $Ru@Mo_2$ > $Fe@Mo_2$ > $Co@Mo_2$ > $Pd@Ti_3$. Among these SACs, MXene supported Ni was shown to possess the lowest overall reaction energy barrier at 0.27 eV followed by Fe (with an overall reaction energy barrier of 0.4 eV),

[a]*School of Chemistry and Chemical Engineering, State Key Laboratory Incubation Base for Green Processing of Chemical Engineering, Shihezi University, Shihezi 832003, China*

[b]*State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: sunzy@mail.buct.edu.cn*

warranting their further synthesis and experimental testing for ECR.

The electro-cycloaddition of CO_2 to generate cyclic carbonates is intriguing because cyclic carbonates can be used as monomers for polycarbonates, electrolytes, and aprotic solvents, among others. Honores *et al.* (**https://doi.org/10.1039/D5SU00100E**) investigated the electrochemical cycloaddition of CO_2 to epoxides utilizing Ni(cyclam)Cl_2 and Co(cyclam)Cl_2Cl as electrocatalysts in 1-butyl-3-methylimidazolium-based ionic liquids (ILs) without addition of any other organic solvents. ILs were shown to facilitate epoxide ring opening and stabilize the reaction species. 1-Butyl-3-methylimidazolium bromide provided high yields while 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide only gave low conversion. Spectroelectrochemical measurements indicated that the halide anions in ILs enhanced carbonate formation. DFT calculations confirmed the important role of the *trans*-I isomer of $[Ni(cyclam)]^+$ in facilitating CO_2 coordination and activation. This work highlights the potential of tetraazamacrocyclic metal complexes for promoting electrochemical carbon capture and transformation in ILs.

Achieving industrially viable and efficient electrocatalysis necessitates the design and development of robust electrolyzers. Soni *et al.* (**https://doi.org/10.1039/D4SU00826J**) demonstrated the integration of thermoelectric generators with reactive carbon electrolyzers to convert captured CO_2 into CO. The thermoelectric generators harnessed waste heat to drive the ECR electrolyzers, thus negating any reliance on external sources of heat. Liquid bicarbonate was used to provide high concentrations of captured CO_2, which improves CO_2 utilization efficiency and contaminant tolerance, addressing the drawbacks of gaseous CO_2 electrolysis. This study shows that by coupling carbon capture and conversion technologies together a viable route to tackle the dual challenges of energy sustainability and decarbonization can be found.

The anodic electrocatalytic oxygen evolution reaction (OER) plays a role for sustainable production of H_2 and other value-added chemicals (Zhang *et al.*[3]). However, the large overpotential and the oxidizing environment at the anode lead to energy loss and stability issues. Coupling DFT calculations and microkinetic modelling provides a way to determine key intermediates, rate-limiting steps (RLS), and reaction pathways, yielding benefits in the screening and rational design of improved OER electrocatalysts. Tripathi *et al.* (**https://doi.org/10.1039/d5su00080g**) showed that the formation of OOH* *via* an Eley-Rideal (ER) mechanism is likely the RLS, consistent with experimental Tafel slope analyses if the interfacial field response of O* and OH* is considered. The desorption of O_2* is unlikely to be rate-limiting.

Iridium oxides (IrO_2/IrO_x) are state-of-the-art electrocatalysts for the OER. There is a growing demand for this rare metal. However, Ir has a low natural abundance (only 0.02 ng g^{-1}) and limited supply (with an annual production <10 tons). This necessitates the development of efficient Ir recycling processes from end-of-life materials (Clapp *et al.*[4]). Turnbull and co-workers (**https://doi.org/10.1039/d5su00038f**) demonstrated a microwave-assisted Ir leaching method from IrO_x. An Ir recovery of up to 83 ± 10% in the form of $IrCl_6^{2-}$ was attained with an extraction condition of low acid concentration ($[H^+]$ = 0.5 M) and moderate temperature (139 °C).

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