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Supporting Information

Catalyst-Electrolyte Interface Chemistry for Electrochemical CO_2 Reduction

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Table S1 Summary on the title, contents, and theme of previous review articles for electrochemical CO_2 reduction. The review articles can be categorized based on main focus: catalyst, electrolyte, cell design & process, mechanism, stability and comprehensive. The number of articles for each group corresponds to 63, 2, 13, 11, 1 and 10 in order.

Ref.	Title	Contents	Theme
This work	Catalyst-Electrolyte Interface Chemistry for Electrochemical CO_2 Reduction	1. Introduction **2. Technoeconomic perspectives of electrochemical CO_2 reduction** 3. Fundamentals of electrochemical CO_2 reduction **4. Design of interfaces between catalyst and surface modulator** 5. Understanding catalyst-electrolyte interfaces 6. Conclusions and perspectives	Control of organic modulators, electrolyte ions, electrode structures and the three-phase boundary at the catalyst-electrolyte interface
1	Advances and challenges in electrochemical CO_2 reduction processes: an engineering and design perspective looking beyond new catalyst materials	1. Introduction 2. Working principles of electrochemical CO_2 reduction 3. Electrolyzer configurations 4. Electrode structure 5. Electrolyte selection 6. pH effects 7. Pressure and temperature effects 8. Summary and outlook	Electrolyzer configuration, electrode structure, electrolyte selection, pH control, and the electrolyzer's operating pressure and temperature
2	A disquisition on the active sites of heterogeneous catalysts for electrochemical reduction of CO_2 to value-added chemicals and fuel	1. Introduction 2. Active Sites in Metal-Based Catalysts 3. Active Sites in Metal-Carbon Catalysts 4. Active Sites in Carbon-Based Catalysts 5. Advanced Tools for Active Site Determination 6. Machine Learning in CO_2RR 7. Summary and Outlook	Design strategies of active sites
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4	An overview on the recent developments of Ag-based electrodes in the electrochemical reduction of CO_2 to CO	1. Introduction 2. Ag-based nanostructured electrode materials 3. Outlook on surface engineering	Material factors in Ag-based electrodes
5	Metal-organic frameworks for electrochemical reduction of carbon dioxide: The role of metal centers	1. Introduction 2. Mechanism of electrocatalytic reduction of CO_2 3. MOFs-based materials for electrochemical reduction of CO_2 4. Conclusions and outlooks	MOF-based electrocatalysts
6	Pushing the activity of CO_2 electroreduction by system engineering	1. Introduction 2. Catalytic reactor design 3. Renewable energy-driven systems 4. System optimization 5. Summary and outlook	Reactor architectures and system engineering
7	Strategies for designing nanoparticles for electro- and photocatalytic CO_2 reduction	1. Introduction 2. Designer Metal Nanoparticles for Electrocatalytic CO_2RR 3. Designer Semiconductor Nanoparticles for Photocatalytic CO_2RR 4. Conclusion and Perspectives	Strategy of designing nanoparticles
8	Rational design of Ag-based catalysts for the electrochemical CO_2 reduction to CO: A review	1. Introduction 2. Fundamentals of ECR 3. Advances in silver-based CO_2-to-CO electrocatalysts	Material factors in Ag-based electrodes

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10	Modelling chemical reactions on surfaces: The roles of chemical bonding and van der Waals interactions	1. Introduction 2. Methods 3. Applications: Modelling chemical reactions on metal surfaces 4. More realistic conditions in chemical reactions 5. Remaining challenges 6. Conclusions	Modelling electrocatalytic reduction of CO_2
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12	Emerging nanostructured carbon-based non-precious metal electrocatalysts for selective electrochemical CO_2 reduction to CO	1. Introduction 2. Metal-free heteroatom-doped carbon materials 3. Transition metal heteroatom codoped carbon materials 4. Carbon-based hybrid materials 5. Summary and outlook	Carbon-based non-precious metal electrocatalysts
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16	Carbon-based catalysts for electrochemical CO_2 reduction	1. Introduction 2. Heteroatoms modification 3. Transition metal- nitrogen- carbon Structure 4. Combination with functional groups 5. Conclusions and outlook	Carbon-based catalysts and synthetic strategy
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99	Theoretical insights into selective electrochemical conversion of carbon dioxide	1. Introduction 2. Challenges of electrochemical CO_2 reduction reactions 3. Strategies to tune intermediate binding 4. Conclusions	Design principles of catalyst and electrolyte based on calculational studies
100	Nickel complexes as molecular catalysts for water splitting and CO_2 reduction	1. Introduction 2. Water splitting 3. Carbon dioxide reduction 4. Conclusions	Nickel complexes as molecular catalysts for water splitting and CO_2 reduction

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