

Perspectives on the Microscopic Principles of Eco-friendly Chemical Engineering[†]

Jianzhong Wu*

*Department of Chemical & Environmental Engineering, University of California, Riverside,
CA 92521, USA*

E-mail: jwu@engr.ucr.edu

Phone: +001 (1) 951 827 2413. Fax: +001 (1) 951 827 5696

Abstract

Chemical engineering is a broad field in terms of the scope of practice but the discipline has been united by a few intellectually coherent principles. Among them, thermodynamics, reaction kinetics and transport phenomena are often considered as the cornerstones, providing support for design and operation of diverse chemical processes for power generation and production of numerous industrial goods including plastics, gasoline and ammonia. Traditionally, these processes use fossil fuels as the raw material and/or energy input and thus are responsible for massive greenhouse gas emissions. As fossil-energy-based processes are deemed phasing out due to environmental concerns, development of alternative routes with renewable energy and sustainable feedstock is calling for the expansion of the knowledge base such that eco-friendly processes can be quantified, controlled and optimized with high precision. This article presents some perspectives on possible engineering developments to accelerate the ongoing paradigm shift from fossil fuels to renewable energy.

[†]Based on a talk presented at Shenyang University of Chemical Technology (SYUCT) in September 2021.

1 Introduction

Enough has been said about the dire consequences of climate change. But so far humanity appears failed to address the looming crisis. According to the most recent report by the U.N. Intergovernmental Panel on Climate Change (IPCC), the world is on track to increase about 14% Greenhouse Gas (GHG) emissions in the next decade rather than, as set out in the Paris Agreement, cutting 45% by 2030 and moving toward net-zero emissions by 2050 in order to limit the temperature rise to 1.5 °C above preindustrial levels. As global industrialization has been essentially driven by the fossil energy for over three hundred years, the transition to renewable energy is not merely a technological challenge. GHG reduction urges international collaboration and drastic social-economical reforms including major commitments from wealthy societies to address the basic needs of developing countries. However, eliminating the root causes of the climate change cannot be achieved without technological breakthroughs. Ultimately, GHG reduction is an engineering problem.

The combustion of fossil fuels for electricity, heat and transport contributes about three quarters of global GHG emissions.¹ A big portion of the remaining may be attributed to the production of steel, cement and ammonia with conventional technologies. Because the bulk part of GHG emissions are affiliated with chemical transformations, it is reasonable to expect that chemical engineering will play a vital role in combating the climate crisis. Historically, chemical engineering is mainly concerned with the transformation of natural resources to energy, materials and chemical products. The transformation often starts with fossil fuels, in concomitant with horrendous GHG emissions during their conversion into heat/electricity or various forms of chemical products and materials important for the industrialized world.

As shown schematically in Figure 1, the industrial production of chemical goods and materials typically entails three stages: i) preparation of reactants, ii) chemical transformation, and iii) product purification.² To optimize the efficiency of energy conversion and chemical transformation, chemical engineers have established fundamental principles that allow for the quantitative design of industrial processes with great precision.³ These principles have been

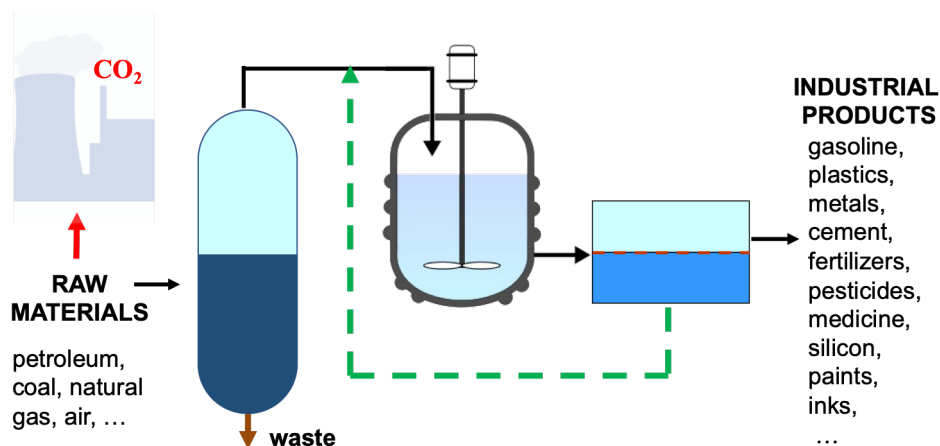


Figure 1: A schematic flowchart for power generation and chemical transformation from raw materials to chemical goods.

used to describe the energy and mass changes during the separation and reactions processes and provide guidelines for the implementation and control of such processes at minimum cost. The core knowledge basis of chemical engineering principles is thermodynamics, reaction kinetics and transport phenomena. As well documented, thermodynamics is related to energy/mass balance for specific chemical processes and the efficiency of chemical and energy conversions. In addition, thermodynamic principles are essential for predicting the physical properties of chemical systems/materials as well as the conditions of phase equilibrium and the reaction extent. Meanwhile, the quantitative descriptions of reaction kinetics and transport phenomena are essential for the design and control of chemical reactions and separation processes.

While humanity’s demand for energy and industrial goods is evergrowing, the manufacturing companies, including chemical industry, have been experiencing a great decline over the past few decades. To illustrate, Figure 2 shows the top 20 U.S. companies ranked by the Fortune magazine.⁴ In 1990, the list is dominated by manufacture with more than half of the top 20 companies affiliated with chemical or petroleum. By contrast, the 2021 list contains only one manufacturing company of industrial goods – Exxon Mobil, which barely maintains its revenue at the 1990 level. Although many industrial goods are no more made

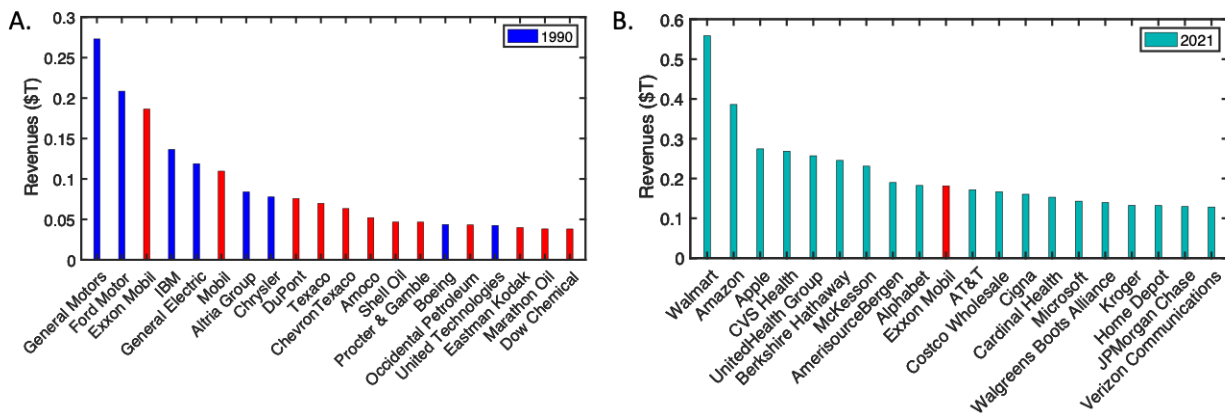


Figure 2: Revenues in 1990 (A) and 2021 (B) for the top 20 American corporations according to FORTUNE 500 rankings. The 1990 numbers have been multiplied by 2.15 to adjust inflation. Color codes: blue for manufacture, red for (petro)chemicals, and teal for all others.⁴

in America, the U.S. GHG emissions decreased merely 7.4% from 1990 to 2020.⁵ The global energy-related CO₂ emission increases from 20.5 Gt in 1990 to 33.0 Gt in 2021 despite the rapid development of renewable energies and the significant improvements of efficiency.⁶

The essential task of GHG reduction is to phase out fossil energy and replace the traditional industrial processes with alternatives that are not just environmentally friendly but economically viable. Toward that end, Figure 3 shows an idealistic sketch for eco-friendly chemical engineering. While renewable energy takes diverse forms in the “carbon-neutral” or “carbon-negative” world, solar power will most likely become a dominant energy source (other than nuclear energy) for both electricity generation and production of industrial goods. The solar-powered processes also involve energy conversion and chemical transformations just like traditional fossil-energy-based chemical processes. Therefore, thermodynamics, reaction kinetics and transport phenomena will inevitably be important in the future production of energy and chemical goods. Different from those based on fossil fuels, however, the alternative processes will be dominated by microscopic operation of energy conversion and chemical transformation rather than bulk reactions and phase equilibrium, entailing new materials for energy storage and catalytic reactions. While fossil fuels have similar atomic building blocks (*viz.*, primarily C and H) and their properties are relatively uniform, the systems underlying

renewable energy conversion and chemical transformation are diverse and many are not yet well established. At present, most existing options for renewable energy are too expensive in comparison with the fossil energy. For cost reduction, extensive data are required for both materials design and process optimization thereby rendering additional challenges. In developing renewable-energy-based chemical processes, cost reduction is particularly important for the industry because implementation of alternative technologies also comes by huge investments on the equipment.

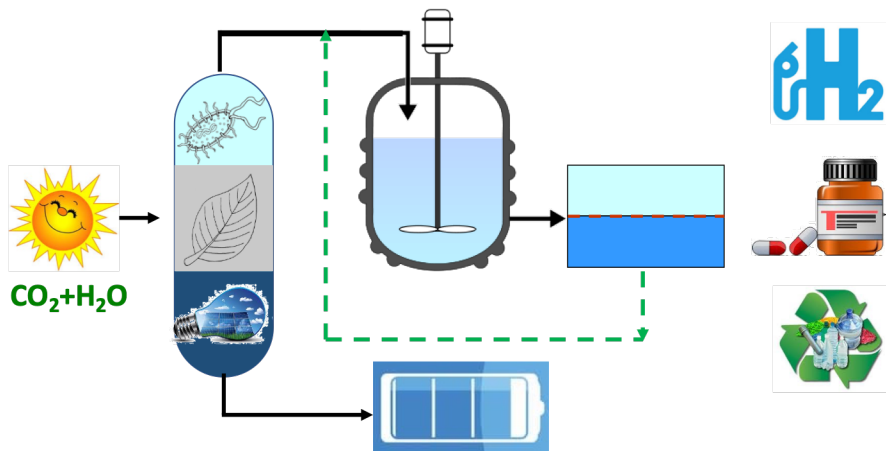


Figure 3: A schematic flowchart for eco-friendly chemical engineering.

The sheer scales of global energy demand and GHG emissions mandate that alternative industrial processes must be suitable for *massive* energy conversion and chemical transformation. To minimize the equipment and operation cost, the carbon-neutral processes must be optimized through quantitative analysis. While traditional chemical engineering principles will no doubt remain relevant to perfect such processes, additional concepts and computational tools are also needed for understanding and, ultimately, prediction and control of, the microscopic details of individual steps underlying materials performance and energy conversion. Toward that end, chemical engineering principles must be endowed with equations to describe renewable energy conversion and storage, relationships between material properties and structure and, most importantly, physicochemical properties dictating the efficiency of chemical conversion and separation. Although the fundamental principles of energy con-

version and chemical transformation have been well established since the beginning of the twentieth century, their application as engineering tools for process and materials design lags far behind. To achieve quantitative performance, the generic equations from quantum and statistical mechanics, which can be used to predict everything in the universe, are often not directly applicable to industrial systems.

The purpose of this article is to discuss possible developments in thermodynamics, reaction kinetics and transport phenomena that may help accelerate the paradigm shift from fossil fuels to renewable energy. By looking over the general procedures of solar energy conversion, electricity storage, and sustainable production of renewable fuels and chemical goods, it highlights some basic concepts and computational tools that will be needed for the quantitative analysis of materials functionality and process optimization.

2 Solar power

Sunlight delivers 1.73×10^5 terawatts (TW) of energy on Earth, which is greater than the global demand (~ 17.7 TW in 2021) by almost 4 orders of magnitude.⁷ While the energy from solar radiation in a single hour is sufficient to power the entire world for more than one year, how much is that energy convertible to electricity or solar fuels for human use? This question is obviously relevant to solar energy utilization but its answer may not be apparent, depending on many factors including the weather conditions and the surface area available for capturing solar energy, in addition to the technical details for converting solar radiation into electrical or chemical energy. One magic power of thermodynamics is that it provides insights into energy conversion and transition among different states of matter even when the microscopic details are unknown.

To illustrate the generic applicability of thermodynamics, Figure 4A shows a schematic diagram for a solar energy converter at steady-state operation. Without any specific knowledge on the apparatus, the first law of thermodynamics asserts that the conversion from

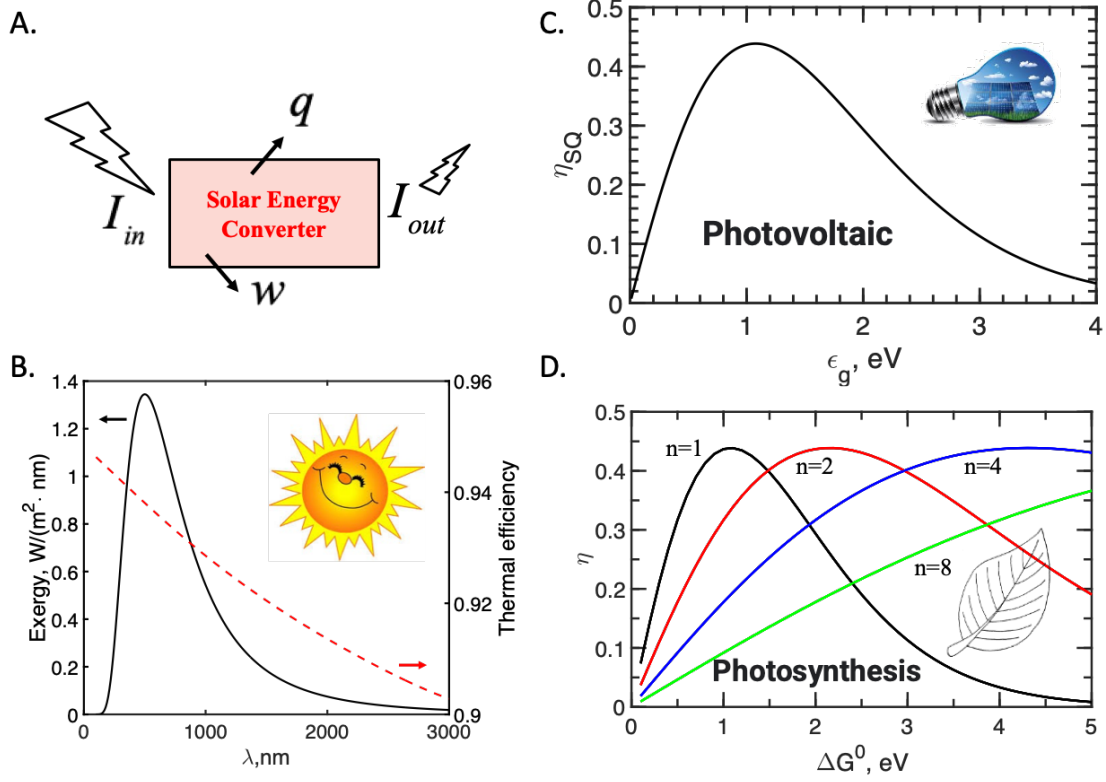


Figure 4: A. A generic device for steady-state solar energy conversion. B. The exergy spectrum of sunlight and the thermodynamic efficiency of conversion to work versus the radio frequency. C. The ultimate efficiency for solar energy conversion by a single threshold solar cell versus the bandgap energy. D. The efficiency of photosynthesis versus the Gibbs energy of reaction ΔG^0 . Here n stands for the number of photons involved in the solar energy conversion.

the radiation energy to heat and work (*viz.*, electrical or chemical energy) must satisfy the balance equation

$$I_{in} = I_{out} + q + w \quad (1)$$

where I_{in} and I_{out} represent the fluxes of radiant energy received and emitted by the device, respectively, q and w are the rates of heat and work generated by the device per unit area of radiation. Meanwhile, the second law prescribes an upper limit for the efficiency of the

energy conversion

$$\eta_P \equiv \frac{w}{I_{\text{in}} - I_{\text{out}}} = 1 - \frac{4}{3} \left(\frac{T_0}{T_S} \right) + \frac{1}{3} \left(\frac{T_0}{T_S} \right)^4 \quad (2)$$

where $T_S \approx 5778$ K represents Sun's surface temperature, and T_0 is the temperature of the device which is assumed in thermal equilibrium with the ambient environment. Eq.(2) is known as the Petela formula, which can be derived from Planck's law of radiation.⁸

Using the average temperature on Earth's surface, $T_0 \approx 288$ K, the second law predicts that the thermodynamic efficiency of solar energy conversion is about 93%, which is remarkably close to the Carnot limit, $\eta_C = 1 - T_0/T_S \approx 0.95$. In addition to this upper limit, thermodynamics provides a quantitative description of the maximum energy convertible to work (*viz.*, exergy) as a function of the radio frequency λ .⁹ As shown in Figure 4B, the exergy profile resembles the solar spectrum, with the energy conversion efficiency falling as the radio wavelength increases.

The above analysis indicates that the solar energy is almost completely convertible into other forms of useful energy (*e.g.*, electricity and fuels). However, under terrestrial conditions, the maximum efficiency of solar energy conversion is significantly smaller, typically less than 30%. The discrepancy between the generic thermodynamic analysis and experimental observations arises from spectrum loss, *i.e.*, there exists a threshold wavelength λ_g beyond which the energy of photons is unable to drive electronic processes for energy conversion owing to the quantum effects. This concept was introduced first by Trivich and Flinn¹⁰ and independently by Shockley and Queisser¹¹ in the context of defining the thermodynamic efficiency of p-n junction solar cells. The spectrum loss reduces the efficiency of solar energy conversion by an additional factor

$$\eta_{\text{PQ}} = \frac{15\beta hc}{\pi^4 \lambda_g} f(\beta hc/\lambda_g) \quad (3)$$

where $\beta \equiv 1/(k_B T)$ with k_B being the Boltzmann constant and T absolute temperature, h

is Planck’s constant, c is the speed of light in vacuum, and $f(x) = x^2\text{Li}_1(e^{-x}) + 2x\text{Li}_2(e^{-x}) + 2\text{Li}_3(e^{-x})$. Figure 4C shows the Shockley–Queisser (PQ) efficiency of solar energy conversion as a function of the bandgap energy ($\epsilon_g = hc/\lambda_g$) for single-threshold solar cells. The thermodynamic analysis provides a key metric in the development of photovoltaic systems because increasing efficiency is a near-linear driver for reducing the cost of solar electricity.¹²

The analysis on spectrum loss is equally applicable to any solar energy conversion processes. For natural or artificial photosynthesis that converts radiation to chemical energy, the threshold wavelength λ_g is determined by the Gibbs energy of reaction (ΔG^0), the number of photons (n) involved in the chemical process, and the energy loss per photon (U_{loss})¹³

$$\lambda_g = \frac{hc}{\Delta G^0/n + U_{\text{loss}}}. \quad (4)$$

Figure 4D shows the maximum energy efficiency for photosynthesis as a function of the Gibbs energy of reaction, ΔG^0 , with the assumption $U_{\text{loss}} = 0$. Because the thermodynamic efficiency depends on the number of photons driving the specific reaction for photosynthesis, a maximum efficiency can be identified by tuning the reaction condition. Although the thermodynamic analysis provides no information on how the process may be achieved in practice, these predictions provide quantitative guidance for the production of energy-rich compounds and the optimal photochemical route for the conversion of solar energy.

The brief discussion above highlights both the generic and specific nature of thermodynamics. The generic nature is easily understood — the fundamental laws of thermodynamics are universally applicable to any energy conversion and chemical transformation processes including those underlying solar energy utilization. The specificity of thermodynamics is more subtle and often not well appreciated; it is manifested, as discussed above, in terms of experimental and/or theoretical procedures for quantifying thermodynamic variables such as ΔG^0 , λ_g and U_{loss} . All thermodynamic variables are system specific. In the context of a comparison between power generation from sunlight and that from fossil fuels, an emphasis on

the specificity of thermodynamics is particularly meaningful. As commonly acknowledged, thermodynamics plays a pivotal role in the design and optimization of steam-power plants and combustion engines, which are currently responsible for more than two-thirds of global CO₂ emissions. In the traditional technology for power generation, the thermodynamic specificity lies, by and large, in the steam tables, which present *experimental data* for the properties of water (*viz.*, steam) at conditions of practical interests. For solar energy conversion, the thermodynamic specificity resides in the properties of photons—the particle representation of solar radiation, and of materials facilitating the energy conversion. Just like that the properties of steam are indispensable for power generation, accurate data for the properties of photons, electrons and materials involved in photosynthesis and electricity generation will be essential for the successful implementation of large-scale solar energy conversion. For the sake of discussion, the results shown in Figure 4 are based on the thermodynamic properties predicted by statistical mechanics for non-interacting photons (*viz.*, ideal photon gas). While the ideal-gas model is remarkably accurate for representing solar radiation, development and utilization of renewable energy for transportation, power generation, and conversion of GHG into useful chemical products require additional data for the properties of underlying thermodynamic systems. Acquisition of such data, by either experimental or theoretical means, should be considered as an engineering task.

3 Energy storage

Petroleum has an energy density (~ 45 GJ/m³) about 30 quadrillion (30×10^{15}) times that of solar radiation, 0.9 trillion (0.9×10^{12}) times that of geothermal energy, and 6.4 billion (6.4×10^9) times that of wind power.¹⁴ These numbers would, at least in part, explain why energy storage was not a serious concern in traditional technology for power generation, transport and industrial production, but it is a formidable challenge when the renewable energy is in widespread use. Apparently, the transition from fossil fuels to renewable energy

sources is not possible without the infrastructure for energy storage on a scale commensurable with the global energy demand.

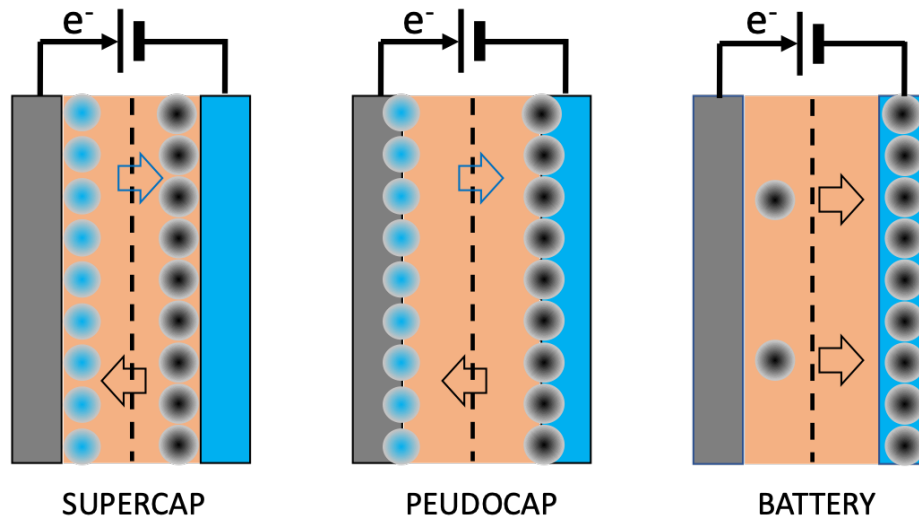


Figure 5: Schematic diagrams for supercapacitor, pseudocapacitor and battery. Here, the blue and grey bars stand for electrodes, the dashed lines represent permeable membrane, the spheres are cations and anions, and electrolyte is shown as background. While ions are physically adsorbed at the electrode surface in a supercapacitor, they are chemically integrated into the electrodes in a battery. A pseudocapacitor involves both ion adsorption and electrochemical reaction.

While energy storage may take diverse forms, the basic concept to convert electricity into other forms of energy is not that complicated.¹⁵ Schematically, Figure 5 illustrates three types of apparatus that are commonly used in electronic devices and will, most likely, be widely adopted as alternatives to combustion engines including those for automobiles. A supercapacitor, or supercap for short, stores energy through the electrosorption of ions onto the surface of porous electrodes. The procedure is not much different from gas adsorption except that, in a supercap, cations and anions are accumulated in different electrodes where the surface charge is balanced by that of counterions. The electrified interface is conventionally known as electric double layer (EDL), which has a capacitance typically larger than that of a parallel dielectric capacitance by several orders of magnitude. For this reason, EDL capacitors are also called supercapacitors. Similar to a supercap, a battery consists of two

electrodes separated by a permeable membrane that prevents short circuits while allows for ion passage during charging and discharging. The main difference between supercap and battery is that the latter entails electrical energy conversion into chemical energy. During the charging process, cations (and/or anions) are generated at one electrode and shuttled to the other with the opposite charge. In a pseudocapacitor, or pseudocap, the energy storage involves both ion adsorption and electrochemical reaction, combining the capabilities of capacitor and battery.¹⁶

Existing technologies for electricity storage are not yet scalable to the massive energy demand. Using the next generation of batteries for transportation vehicles as an example, the U.S. Department of Energy sets specific goals in terms of the charging time (<15 minutes), driving distance (> 300 miles) and cost (\$100-80/kWh). To meet these targets, technological improvements cannot be achieved without understanding the microscopic details of electrochemical processes dictating the power and energy density. For quantitative analysis, we also need thermodynamic and kinetic models to describe the dependence of charging behavior on operation conditions as well as the characteristics of electrolyte, electrodes and separator. Whereas energy transfer and chemical transformation are ubiquitous in traditional chemical engineering processes, the macroscopic models are mostly not applicable to electrochemical phenomena in the micropores of electrodes as commonly adopted for energy storage and electrochemical synthesis.

Like gas adsorption, capacitive energy storage is mostly based on porous materials such as activated carbon. A key quantity of practical interest is capacitance, $C \equiv Q/E$, where Q is the net charge accumulated at the electrode surface, and E is the applied voltage. The electrode charge is balanced by that of ionic species distributed near the surface according to the Boltzmann equation¹⁷

$$\rho_i(\mathbf{r}) = \rho_i^0 \exp \left[-\beta Z_i e \psi(\mathbf{r}) - \beta \Delta \mu_i^{\text{ex}}(\mathbf{r}) - \beta \varphi_i^{\text{ext}}(\mathbf{r}) \right]. \quad (5)$$

In Eq.(5), ρ_i^0 stands for the concentration of ionic species i in the bulk solution, Z_i is the ion valence, e represents unit charge, $\psi(\mathbf{r})$ is the local electrical potential, $\Delta\mu_i^{\text{ex}}(\mathbf{r})$ represents the deviation of the local excess chemical potential from the bulk value, and $\varphi_i^{\text{ext}}(\mathbf{r})$ denotes a non-electrostatic potential due to the ion-electrode interactions. While the local electrical potential can be calculated from the ionic density profiles by using the Poisson equation, microscopic models for the ionic species and electrodes are needed in order to quantify $\mu_i^{\text{ex}}(\mathbf{r})$ and $\varphi_i^{\text{ext}}(\mathbf{r})$, which account for ion-ion correlation effects and ion-electrode interactions, respectively. These functions are intimately linked with the chemical details of the electrolyte and electrode materials thereby dictating the device performance.¹⁸ Without these two terms on the right side, Eq.(5) reduces to the Poisson–Boltzmann equation, which is commonly used to describe ion distributions near a charged surface. The density profiles of ionic species can be predicted with various statistical-thermodynamic models.¹⁹ Molecular modeling provides a understanding, and eventually a quantitative description of, the device performance in terms of the diverse parameters of the electrolyte and electrodes including the pore geometry, pore size distribution, solvent composition, ion valence and concentration.

For an electrochemical battery, both the voltage and capacity are related to the Gibbs energies of electrode reactions underlying the energy conversion. For example, the open circuit voltage of a lithium–ion battery can be predicted from the difference between the chemical potentials of Li atoms within the cathode and the anode²⁰

$$E_{OC} = \frac{\mu_{\text{Li (anode)}} - \mu_{\text{Li (cathode)}}}{e}. \quad (6)$$

For a battery with the metallic lithium as the anode and a multi-metal oxide as the cathode, the chemical potential of Li atoms in the anode is the same as the molar Gibbs energy of Li metal, and that for the cathode can be predicted from first-principle calculations in combination with Monte Carlo simulation.²¹ For cathode discharging from $\text{Li}_{x_1}\text{MO}_2$ to $\text{Li}_{x_2}\text{MO}_2$, where M denotes 3d transition metals (*e.g.*, Co or Mn), the maximum electrical

work per unit of MO_2 can be obtained by the integration of the voltage times the displaced charge:

$$W = \int_{x_1}^{x_2} [\mu_{\text{Li (anode)}} - \mu_{\text{Li (cathode)}}] dx_{\text{Li}}. \quad (7)$$

In principle, the procedure can be similarly applied to pseudocapacitors, albeit the computation is more challenging because the evolution of the atomic structure with the degree of charging is mostly known.²²

In addition to thermodynamic considerations, reaction kinetics and transport phenomena are also important for energy storage because they determine the power density, charging time and heat management, among other things. The dynamics of electrochemical processes is conventionally described by volume-averaged porous electrode models.²³ The macroscopic methods provide a powerful mathematical framework to analyze the influence of electrode porosity, conductivity, and surface reactions on electrokinetic phenomena. However, they offer little insight into the transport, distribution, and surface reactions of ionic species in the micropores of electrodes underlying electrosorption and charge transfer. Besides, the traditional electrokinetic models take drastic approximations for the EDL structure and often employ a large number of semi-empirical parameters. Over the past few decades, many microscopic models have been developed to describe ion transport and the kinetics of electrochemical reactions. For ion transport through the micropores of an electrode, the governing equation can be written as²⁴

$$\frac{\partial \rho_i(\mathbf{r}, t)}{\partial t} = D_i \nabla^2 \rho_i(\mathbf{r}, t) + \nabla \cdot \beta D_i \rho_i(\mathbf{r}, t) \nabla [Z_i e \psi(\mathbf{r}, t) + \mu_i^{\text{ex}}(\mathbf{r}, t) + \varphi_i^{\text{ext}}(\mathbf{r})] + \rho_i(\mathbf{r}, t) \mathbf{v}_0(\mathbf{r}, t) \quad (8)$$

where D_i denotes ion diffusivity. The first term on the right side of Eq.(8) accounts for ion diffusion, the second term represents electromigration, and the last term arises from the ion flux in a net flow with solvent velocity \mathbf{v}_0 . The flow effect can be accounted for by solving Eq.(8) along with the Navier-Stokes equation.²⁵ If we ignore thermodynamic non-ideality

due to ion-ion correlations and non-electrostatic ion-electrode interactions, $\mu_i^{ex} = \varphi_i^{ext} = 0$, and Eq.(8) reduces to the time-dependent form of the Nernst-Planck (NP) equation which is commonly used to describe macroscopic ion transport.²⁶

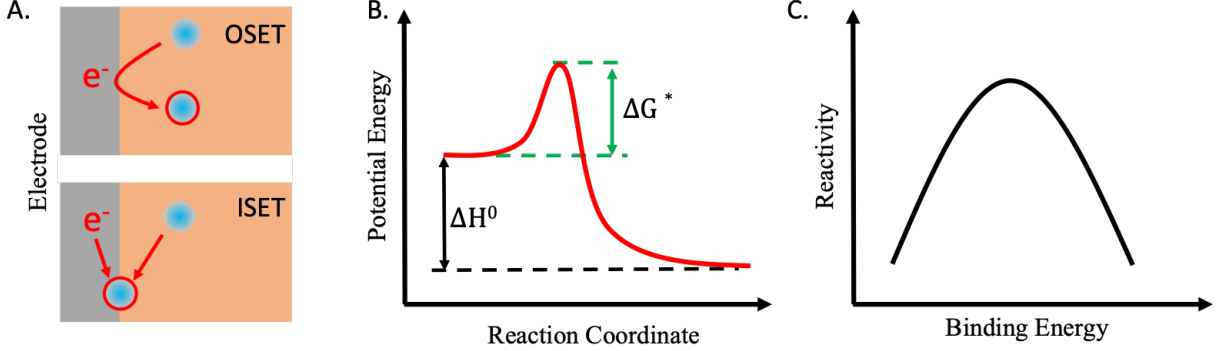


Figure 6: A. Two basic modes of electron transfer between an electrode and a chemical species from the electrolyte solution. The outer-sphere electron transfer (OSET) involves an electron tunneling across the electric double layer, while the inner-sphere electron transfer (ISET) results in bond formation. B. The kinetics of OSET as depicted by the transition-state theory. C. The volcano-like relationship between the rate of ISET and the surface binding free energy.

Conventionally, the kinetics of electrochemical reactions is described by the Butler-Volmer (BV) equation.²⁷ For a unimolecular process $O + e^- \rightarrow R$, the reaction rate is given by

$$v = -k_0 e^{-\alpha\beta e(E-E_f^0)} C_R + k_0 e^{(1-\alpha)\beta e(E-E_f^0)} C_O \quad (9)$$

where C_R and C_O are the concentrations of the reactive species in reduced and oxidized states, respectively, and E denotes the electrode potential. With the standard heterogeneous rate constant (k_0), the transfer coefficient (α), and the formal potential (E_f^0) treated as adjustable parameters, the BV equation provides a satisfactory description of the reaction rate for many electrochemical systems.²⁶ However, the semi-empirical approach yields limited physical insight in terms of the nature of the electroactive molecules, the medium, and the microscopic details of the electrode. As illustrated in Figure 6, an electrode reaction may take place through different mechanisms of electron transfer. In OSET, an electron transfers from the electrode to a chemical species in the electrolyte solution by tunneling. In this case,

the surface chemistry of the electrode is largely inconsequential. The rate of reaction can be predicted by the Marcus–Hush theory.²⁸ In ISET, the reactive species binds with the electrode analogous to bond formation during intermolecular reactions. In both cases, theoretical investigations hinge on quantum-mechanical predictions of thermodynamic quantities such as the activation free energy and surface binding energy. While a molecular theory of ISET reactions has yet to be developed, the binding energy provides a useful descriptor for understanding and quantifying surface reactions involving electrocatalysis (*e.g.*, via volcano-like relationship).²⁹ The linkage between these physical quantities and device performance thus provides a theoretical basis for understanding, design, and optimization of energy storage processes.

4 Sustainable chemical production

Commodity chemicals and materials are keystones of modern society. While traditional manufacturing processes for many industrial products are notoriously energy intensive and responsible for major CO₂ emissions, eco-friendly, cost-effective alternatives have yet to be fully developed. Nevertheless, as illustrated by Figure 7, the desired solution is clear, *i.e.*, industrial-scale production of iron, ammonia, hydrogen and, possibly, liquid fuels such as methanol, via electrochemical reduction. While the electrochemical approaches have been known for years (*e.g.*, hydrogen was generated from electricity as early as 1789³⁰), what have been holding them back for widespread industrial applications?

Steel production is one of the most energy and CO₂ intensive industrial processes, accounting for about 8% of the global energy use and 10% of GHG emissions.³¹ Possible alternatives for steelmaking include electrolysis and hydrogen reduction. The electrolytic process was proposed by a French metallurgist, Paul Héroult, as early as 1906. The essential

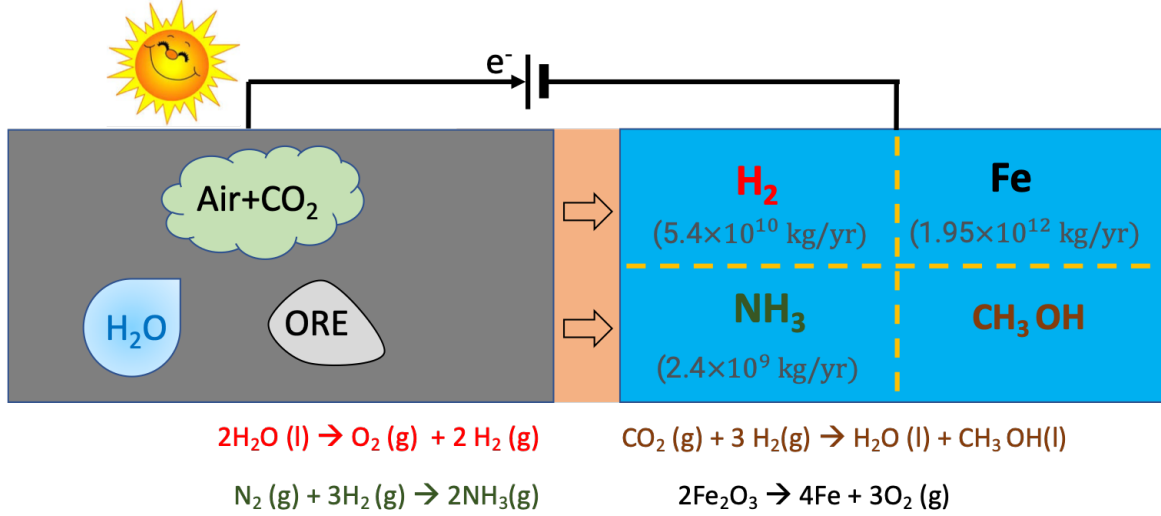
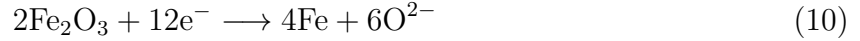


Figure 7: Four chemical species – hydrogen, iron, ammonia and methanol – dominating the sustainable production of commodity chemicals and materials.

idea was metal deposition from molten iron oxide at the cathode



concomitant with the formation of oxygen gas at the anode



The electrochemical process occurs at about 1,600 °C, which is significantly lower than the temperature inside blast furnaces for traditional steelmaking (>2,000 °C). In comparison with the traditional method, the electrolytic approach reduces energy use by almost one third and cuts CO₂ emissions by 87%.

Whereas the cathode and anode reactions for iron oxide reduction are nothing special in comparison with those of ordinary electrochemical processes, engineering development of the electrolytic process faces a multitude of challenges.³² A major hurdle has been the absence of design criteria for selecting electrode materials and optimizing the composition of molten oxides that may be suitable to be used as the electrolyte. In particular, thermodynamic

considerations are necessary to avoid the dissolution of electrodes into liquid metal or molten oxide and prevent the use of materials that are more reactive than the metal target. While a combination of thermodynamic analysis and kinetic predictions will provide guidelines for materials selection, the task is not possible without extensive experimental data and robust theoretical tools to describe the materials behavior and the physical properties of molten oxides. These bottlenecks attribute to the slow progress in developing the electrolytic process for mass production of steel. On the one hand, the thermodynamic and transport properties of molten oxides remain poorly understood, and a theoretical description has yet to be developed to account for network formation among metal and oxygen atoms. On the other hand, the thermal effects are ignored in conventional electronic theories but important for describing the electrode reactions at high temperature.

The hydrogen-based route for steelmaking also eschews CO₂ emission but the process is less energy efficient than electrolysis. Besides, conventional methods for hydrogen production are mostly based on coal gasification or methane steam reforming that are not environmentally friendly. Green hydrogen may be achievable through water electrolysis or hydrocarbon/biomass pyrolysis.³³ Despite a long history of technological progress and substantial developments over the past few decades in understanding the fundamental mechanisms of hydrogen and oxygen evolution reactions, water electrolysis – with either alkaline diaphragm or proton-exchange membrane – remains economically uncompetitive because of the limited charge density, the use of expensive catalysts, and/or the lack of membranes conducting hydroxyl ions.³⁴ For industrial-scale hydrogen production, the biomass/hydrocarbon conversion technologies are free of electricity but similar challenges exist in terms of the lack of predictive tools for process development and cost reduction.³⁵

With near 200 million metric tons of annual production rate, ammonia is an iconic chemical product, important not only for making fertilizers but also for pharmaceuticals, plastics, textiles, explosives, and numerous other chemicals containing nitrogen atoms.³⁶ The revered Haber-Bosch process converts nitrogen and hydrogen into ammonia over an

iron catalyst with intensive energy input (>30 GJ/ton NH_3) and extensive GHG emissions (~ 2.16 kg CO_2 -eq/kg NH_3). A wide range of alternative approaches have been proposed to make ammonia synthesis sustainable, including electrochemical, photocatalytic and biological methods.³⁷ While these alternative methods use significantly less energy and free of CO_2 emissions, the challenge is again to scale up and reduce the cost such that the carbon-free processes would become commercially competitive. Toward that end, experimental data and thermodynamic/kinetic models will be necessary for understanding and, ultimately, controlling the electrochemical evolution of hydrogen and nitrogen atoms at the surface of electrode or catalyst.

One potential game changer in combating global climate change is development of large-scale industrial processes that use CO_2 as a feedstock for the production of materials, fuels and chemical commodities.³⁸ Possible strategies include electrocatalytic conversion of CO_2 to renewable fuels such as methanol or aviation fuels,³⁹ transformation of CO_2 to organic molecules such as cyclic carbonates, carbamates and ureas,⁴⁰ and the use of CO_2 to produce polymers such as polycarbonates, polyols, polyurethanes, polyureas and polyesters.⁴¹ In general, CO_2 reduction is a complex process that involves multiple phases and a large number of chemical species and elementary reactions. Over the past few decades, numerous theoretical studies have been devoted to understanding the reaction mechanisms and pathways for CO_2 conversion to various chemical products.^{42,43} Previous research indicates that different catalysts for CO_2 reduction lead to different chemical products and conversion efficiency. Therefore, catalyst design plays an essential role to make the CO_2 conversion processes commercially viable.

Whereas significant progress has been made toward understanding the initial steps of CO_2 reduction at idealized catalytic surfaces, major challenges remain for a comprehensive description of both reaction and transport processes under conditions consistent with experimental investigations. Existing calculations of CO_2 reduction mostly ignore the kinetic barriers, solvent effects, and the potential dependence in constructing reaction pathways.

To fully understand the reaction mechanism under real catalytic conditions, new computational strategies are needed to integrate reaction-network simulation and transport modeling. Recent advances in the fields of theoretical and computational chemistry along with the ever-increasing computational capability have made it possible to explore the chemical space in terms of a massive reaction network with an explicit consideration of all potentially relevant molecular structures.⁴⁴ Furthermore, machine-learning methods can be utilized to attain an in-depth understanding of all reaction pathways and, more important, a quantitative description of the chemical evolution over time given a set of initial conditions (*e.g.*, reactants and their concentrations, temperature, and surface voltage).⁴⁵ The data-driven approach also provides a powerful means to inverse design of electrode materials and catalysts with improved chemical reactivity. A thorough and accurate description of reaction pathways are particularly important to promote formation of high-value products such as olefins or benzene from CO₂ reduction by optimizing activity and selectivity.

5 Summary and perspectives

Whereas global climate change mandates that the world must restrict GHG emissions during power generation and industrial production, the development of sustainable alternatives is a massive engineering challenge: The volumetric energy density of coal is sixteen quadrillion times that of sunlight and one billion times that of wind and water power; the Haber-Bosch process for ammonia synthesis represents one of the greatest inventions in human history, enabling food production for almost eight billion people on Earth; petroleum refinery has been optimized near perfection, fueling over one billion automobiles running on the streets and roads; and the chemistry of steelmaking with blast furnaces has remained essentially unchanged for millennia. Why do we believe that all these greatest technological marvels will be eventually substituted with alternatives? The answer is definite — because inaction would result in catastrophic consequences, jeopardizing the entire future of humankind.

Empowered with the fundamental principles of energy conversion and chemical transformation, chemical engineering is in a unique position to facilitate swift transition from fossil fuels to renewable energy. Since the profession was created in the late 19th century, chemical engineers have been playing a key role in design and optimization of industrial processes for both power generation and mass production of fuels and commodity goods. It is unimaginable that alternative processes for energy and chemical production would be established without their contributions.

However, chemical engineering is no magic. Although chemical engineering principles are founded on the fundamentals of science and technological innovations, the profession is distinguished from scientific disciplines such as physics, chemistry and biology because it is rooted in industrial applications. Qualitative understanding is not enough for efficient engineering design. Steam tables have been used as a blueprint for power generation and industrial heating not because they are elegant or scientifically most advanced but because they provide reliable experimental data to quantify the underlying processes for energy conversions. By the same token, cubic equations of state are important for oil refinery because they allow for the accurate prediction of the vapor-liquid phase diagrams of petroleum systems, not because they are scientifically most rigorous in describing the thermodynamic properties of liquid mixtures with myriad chemical species and complicated intermolecular interactions.

But steam tables are of no use for the conversion of sunlight to electricity or solar fuels. A cubic equation of state cannot describe ion adsorption in the micropores of electrodes, the free energies of cathode materials in lithium ion batteries, or the solubility of iron in molten oxides. To phase out fossil fuels and replace them with renewable feedstock, new experimental data and equations are needed to design, implement and control energy conversion, reaction and separation processes that involve complicated chemical systems totally different from steam or petroleum. While the mission remains the same, chemical engineering principles must be augmented with additional knowledge that can be used to quantify not only

energy and mass balance at the macroscopic scales but also the microscopic structure, thermodynamics, kinetics and transport phenomena underlying renewable energy conversion and chemical transformation. The quantitative descriptions, in terms of either experimental data or computational models, are inevitable for industrial production of materials, chemicals and energy.

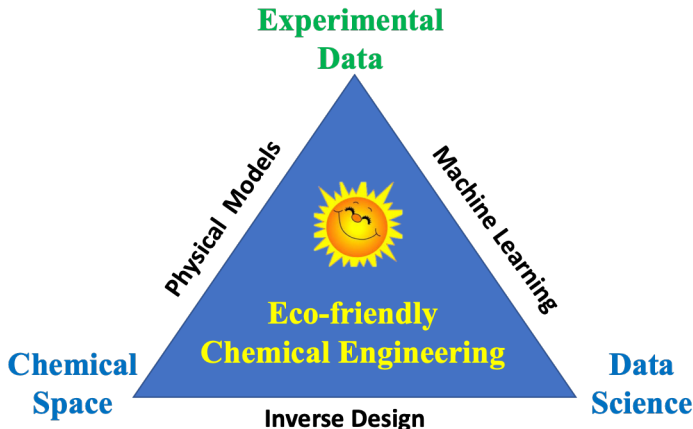


Figure 8: Augmenting the fundamentals of chemical engineering with microscopic principles and data science.

Looking into the future, we expect that chemical engineering will continue to thrive by embracing new principles for engineering design and optimization of chemical processes with no harm to the environment. Toward that end, Figure 8 sketches a triangular relationship among the chemical space for industrial goods, experimental data, and data-science models for chemical design and exploration. While experimentation will no doubt dominate the engineering practice, computational tools are essential to accelerate the pace of transition towards renewable energy sources. The computing power, now capable of a quintillion (10^{18}) calculations each second and yet even faster with quantum computers, gives us confidence that humanity will overcome the enormous challenges to replace fossil fuels with renewable energy before the climate apocalypse.

References

- (1) Pörtner, H.-O., Roberts, D., Tignor, M., Poloczanska, E., Mintenbeck, K., Alegría, A., Craig, M., Langsdorf, S., Löschke, S., Möller, V., A. Okem, B. R., Eds. *Climate Change 2022: Impacts, Adaptation, and Vulnerability*; Cambridge University Press, 2022.
- (2) Prausnitz, J. M. Abstraction and Reality. The Two Sources of Chemical Thermodynamics. **1986**, *11*, 49–66.
- (3) Varma, A.; Grossmann, I. E. Evolving trends in chemical engineering education. *AIChE Journal* **2014**, *60*, 3692–3700.
- (4) <https://fortune.com/fortune500/>, Fortune 500. *Fortune Magazine* **2022**,
- (5) <https://www.epa.gov/ghgemissions/draft-inventory-us-greenhouse-gas-emissions-and-sinks-1990-2020>, Draft Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2020. *The U.S. Environmental Protection Agency* **2022**,
- (6) <https://www.iea.org/data-and-statistics/charts/global-energy-related-co2-emissions-1990-2021>, Global energy-related CO₂ emissions, 1990-2021. *International Energy Agency* **2022**,
- (7) Crabtree, G. W.; Lewis, N. S. Solar energy conversion. *Physics Today* **2007**, *60*, 37–42.
- (8) Petela, R. Exergy of undiluted thermal radiation. *Solar Energy* **2003**, *74*, 469–488.
- (9) Delgado-Bonal, A. Entropy of radiation: the unseen side of light. *Scientific Reports* **2017**, *7*, 1642.
- (10) Trivich, D.; Flinn, P. In *Solar Energy Research*; Daniels, F., Duffie, J., Eds.; Thames and Hudson: London, 1955; Chapter Maximum efficiency of solar energy conversion by quantum processes, p 143.

- (11) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *Journal of Applied Physics* **1961**, *32*, 510–519.
- (12) Ehrler, B.; Alarcón-Lladó, E.; Tabernig, S. W.; Veeken, T.; Garnett, E. C.; Polman, A. Photovoltaics Reaching for the Shockley–Queisser Limit. *ACS Energy Letters* **2020**, *5*, 3029–3033.
- (13) Bolton, J. R.; Haught, A. F.; Ross, R. T. In *Photochemical Conversion and Storage of Solar Energy*; Connolly, J. S., Ed.; Academic Press, 1981; pp 297–339.
- (14) Layton, B. E. A Comparison of Energy Densities of Prevalent Energy Sources in Units of Joules Per Cubic Meter. *International Journal of Green Energy* **2008**, *5*, 438–455.
- (15) Winter, M.; Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? *Chemical Reviews* **2004**, *104*, 4245–4270.
- (16) Fleischmann, S.; Mitchell, J. B.; Wang, R.; Zhan, C.; Jiang, D.-e.; Presser, V.; Augustyn, V. Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials. *Chemical Reviews* **2020**, *120*, 6738–6782.
- (17) Wu, J. Density functional theory for chemical engineering: From capillarity to soft materials. *AIChE Journal* **2006**, *52*, 1169–1193.
- (18) Shao, H.; Wu, Y.-C.; Lin, Z.; Taberna, P.-L.; Simon, P. Nanoporous carbon for electrochemical capacitive energy storage. *Chemical Society Reviews* **2020**, *49*, 3005–3039.
- (19) Zhan, C.; Lian, C.; Zhang, Y.; Thompson, M. W.; Xie, Y.; Wu, J.; Kent, P. R. C.; Cummings, P. T.; Jiang, D.-e.; Wesolowski, D. J. Computational Insights into Materials and Interfaces for Capacitive Energy Storage. *Advanced Science* **2017**, *4*, 1700059.
- (20) Aydinol, M. K.; Kohan, A. F.; Ceder, G.; Cho, K.; Joannopoulos, J. Ab initio study of lithium intercalation in metal oxides and metal dichalcogenides. *Phys. Rev. B* **1997**, *56*, 1354–1365.

- (21) Meng, Y. S.; Arroyo-de Dompablo, M. E. First principles computational materials design for energy storage materials in lithium ion batteries. *Energy & Environmental Science* **2009**, *2*, 589–609.
- (22) Fleischmann, S.; Zhang, Y.; Wang, X.; Cummings, P. T.; Wu, J.; Simon, P.; Gogotsi, Y.; Presser, V.; Augustyn, V. Continuous transition from double-layer to Faradaic charge storage in confined electrolytes. *Nature Energy* **2022**,
- (23) Newman, J. S.; Balsara, N. P. *Electrochemical Systems*, 4th ed.; Wiley: Hoboken, NJ, 2019.
- (24) te Vrugt, M.; Löwen, H.; Wittkowski, R. Classical dynamical density functional theory: from fundamentals to applications. *Advances in Physics* **2020**, *69*, 121–247.
- (25) Kong, X.; Jiang, J.; Lu, D.; Liu, Z.; Wu, J. Molecular Theory for Electrokinetic Transport in pH-Regulated Nanochannels. *The Journal of Physical Chemistry Letters* **2014**, *5*, 3015–3020.
- (26) Batchelor-McAuley, C.; Kätelhön, E.; Barnes, E. O.; Compton, R. G.; Laborda, E.; Molina, A. Recent Advances in Voltammetry. *ChemistryOpen* **2015**, *4*, 224–260.
- (27) Dickinson, E. J.; Wain, A. J. The Butler-Volmer equation in electrochemical theory: Origins, value, and practical application. *Journal of Electroanalytical Chemistry* **2020**, *872*, 114145.
- (28) Chidsey, C. E. D. Free Energy and Temperature Dependence of Electron Transfer at the Metal-Electrolyte Interface. *Science* **1991**, *251*, 919–922.
- (29) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, eaad4998.

- (30) Smolinka, T.; Bergmann, H.; Garche, J.; Kusnezoff, M. In *Electrochemical Power Sources: Fundamentals, Systems, and Applications*; Smolinka, T., Garche, J., Eds.; Elsevier, 2022; pp 83–164.
- (31) Peplow, M. Can industry decarbonize steelmaking? *Chemical & Engineering News* **2021**, *99*, <https://cen.acs.org/environment/green-chemistry/steel-hydrogen-low-co2-startups/99/i22>.
- (32) Allanore, A. Features and Challenges of Molten Oxide Electrolytes for Metal Extraction. *Journal of The Electrochemical Society* **2014**, *162*, E13–E22.
- (33) Liu, W.; Zuo, H.; Wang, J.; Xue, Q.; Ren, B.; Yang, F. The production and application of hydrogen in steel industry. *International Journal of Hydrogen Energy* **2021**, *46*, 10548–10569.
- (34) Yue, M.; Lambert, H.; Pahon, E.; Roche, R.; Jemei, S.; Hissel, D. Hydrogen energy systems: A critical review of technologies, applications, trends and challenges. *Renewable and Sustainable Energy Reviews* **2021**, *146*, 111180.
- (35) Ishaq, H.; Dincer, I. Comparative assessment of renewable energy-based hydrogen production methods. *Renewable and Sustainable Energy Reviews* **2021**, *135*, 110192.
- (36) FAO, *World fertilizer trends and outlook to 2022*; The Food and Agriculture Organization of the United Nations, 2020; p 34.
- (37) Ghavam, S.; Vahdati, M.; Wilson, I. A. G.; Styring, P. Sustainable Ammonia Production Processes. *Frontiers in Energy Research* **2021**, *9*, 1–15.
- (38) Seidler, J.; Strugatchi, J.; Gärtner, T.; Waldvogel, S. R. Does electrifying organic synthesis pay off? The energy efficiency of electro-organic conversions. *MRS Energy & Sustainability* **2021**, *7*, 42.

- (39) Schlögl, R. Chemical Batteries with CO₂. *Angewandte Chemie International Edition* **2022**, *61*, e202007397.
- (40) Fu, H.-C.; You, F.; Li, H.-R.; He, L.-N. CO₂ Capture and in situ Catalytic Transformation. *Frontiers in Chemistry* **2019**, *7*, 1–15.
- (41) Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C. Advances in the use of CO₂ as a renewable feedstock for the synthesis of polymers. *Chem. Soc. Rev.* **2019**, *48*, 4466–4514.
- (42) Xu, S.; Carter, E. A. Theoretical Insights into Heterogeneous (Photo)electrochemical CO₂ Reduction. *Chemical Reviews* **2019**, *119*, 6631–6669.
- (43) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F.; Chorkendorff, I. Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chemical Reviews* **2019**, *119*, 7610–7672.
- (44) Unsleber, J. P.; Reiher, M. The Exploration of Chemical Reaction Networks. *Annual Review of Physical Chemistry* **2020**, *71*, 121–142.
- (45) Keith, J. A.; Vassilev-Galindo, V.; Cheng, B.; Chmiela, S.; Gastegger, M.; Müller, K.-R.; Tkatchenko, A. Combining Machine Learning and Computational Chemistry for Predictive Insights Into Chemical Systems. *Chemical Reviews* **2021**, *121*, 9816–9872.

TOC Graphic

