This is an open access article published under a Creative Commons Attribution (CC-BY) <u>License</u>, which permits unrestricted use, distribution and reproduction in any medium, provided the author and source are cited.

# PHYSICAL CHEMISTRY



## Building Blocks for High Performance in Electrocatalytic CO<sub>2</sub> Reduction: Materials, Optimization Strategies, and Device Engineering

Gastón O. Larrazábal, Antonio J. Martín, and Javier Pérez-Ramírez\*0

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland

**Supporting Information** 

**ABSTRACT:** In recent years, screening of materials has yielded large gains in catalytic performance for the electroreduction of  $CO_2$ . However, the diversity of approaches and a still immature mechanistic understanding make it challenging to assess the real potential of each concept. In addition, achieving high performance in  $CO_2$  (photo)electrolyzers requires not only favorable electrokinetics but also precise device engineering. In this Perspective, we analyze a broad set of literature reports to construct a set of design—performance maps that suggest patterns between performance figures and different classes of materials and optimization strategies. These maps facilitate the screening of different approaches to electrocatalyst design and the identification of promising avenues for future developments. At the device level, analysis of the network of limiting phenomena in (photo)electrochemical cells leads us to propose a straightforward performance metric based on the concepts of maximum energy efficiency and maximum product formation rate, enabling the comparison of different technologies.



The combination of the electrochemical reduction of  $CO_2$  (eCO<sub>2</sub>RR) with carbon-neutral energy sources is an attractive approach for valorizing CO<sub>2</sub> emissions while contributing to close the anthropogenic carbon cycle.<sup>1</sup> However, despite recent advances, the practical realization of this reaction still requires the development of catalysts that show high selectivity toward a *single* eCO<sub>2</sub>RR product at low overpotentials while inhibiting the competing hydrogen evolution reaction (HER). In addition, significant efforts on the engineering of functional electrolyzers that integrate CO<sub>2</sub> reduction with a suitable anodic reaction are still needed.<sup>2</sup>

Despite recent advances, the practical realization of the electrochemical reduction of CO<sub>2</sub> still requires development of catalysts that show high selectivity toward a *single* eCO<sub>2</sub>RR product at low overpotentials while inhibiting the competing hydrogen evolution reaction.

Pioneering studies in the 1980s and 1990s established a basic classification, based on the product selectivity of different transition and post-transition bulk metal electrodes, that has helped guide the development of catalysts for the  $eCO_2RR$ .<sup>3,4</sup> At a molecular level, the performance of a  $CO_2$  reduction

electrode is defined not only by the identity of the material used as catalyst but also by the optimization strategy that has been applied to tune the architecture of the catalyst and/or its surrounding electrochemical environment. For example, controlling the size and morphology of metal nanoparticles<sup>5</sup>, (i.e., a structural modification) and the addition of an ionic liquid to the electrolyte<sup>7</sup> (i.e., thus modifying the reaction environment) have been shown to enhance the eCO2RR performance of different materials. However, different approaches to catalyst design are rarely compared to each other, making it challenging to identify what combinations of materials and strategies are particularly successful. In this context, this Perspective aims to provide tools to uncover design-performance trends in terms of practical parameters and facilitate the comparison of different approaches. While this screening is valuable for identifying new avenues for catalyst development, a more rational design of eCO2RR catalysts demands a deeper understanding of the relationship between materials, strategies, and the reaction mechanism. Consequently, we have aimed to provide such mechanistic insights whenever available, and we highlight the role of detailed electrokinetic studies and of in situ and operando experimental studies, complemented by theoretical efforts, in the development of performance descriptors.

In regard to practical devices, recent studies have assessed the performance gaps (for different products) that separate the

Received: June 1, 2017 Accepted: August 1, 2017 Published: August 1, 2017

eCO<sub>2</sub>RR from economic viability.<sup>2,8</sup> Although catalyst stability remains a major hurdle (i.e., thousands of operating hours are required), state-of-the-art electrolyzers producing CO and (particularly) HCOO<sup>-</sup> show cell voltages (below 2.5 V) and current densities  $(100-200 \text{ mA cm}^{-2})$  that are encouragingly close to practical thresholds. Because mass and charge transport add to electrokinetics to deviate performance away from ideality, understanding the relationship between electrolyzer design and limiting phenomena under different operation conditions is of great importance.<sup>9</sup> Moreover, there is a lack of standard metrics, which is prerequisite for proper assessment of available technologies. In the final section of this Perspective, we associate the performance of a device to its energy efficiency and product formation rate. Following a description of the main limiting phenomena, we propose a simple and robust performance metric to characterize reported photo- and electrolyzers, shedding light on the challenges faced by the eCO<sub>2</sub>RR to become a competitive process.

Product-Performance Map of Electrochemical CO<sub>2</sub> Reduction. In the first part of this Perspective, we aim to facilitate the identification of design-performance trends in CO<sub>2</sub> reduction catalysis using widely accessible experimental parameters for the analysis. To this end, we first extracted the maximum faradaic efficiency (FE) (toward a CO<sub>2</sub> reduction product) and its corresponding overpotential (calculated as the difference between the reported cathodic potential and the standard reduction potential) from ~160 reports in the literature. Considering the multiproduct nature of the eCO2RR and the existence of different reaction mechanisms, this criterion is a straightforward starting point for assessing catalyst performance because high selectivities at low overpotentials are indicative of electrocatalysts that are both efficient at storing energy in the target CO<sub>2</sub> reduction product (avoiding energy losses to the unwanted HER) and successful at steering the reaction through several possible pathways. When represented on a map, the comparison of data sets associated with each product revealed some general trends (Figure 1). A cluster analysis of the points (by kernel density estimation, KDE) unequivocally revealed performance regions associated with each product. To summarize, a relatively large number of electrocatalytic systems have been reported to produce CO and HCOO<sup>-</sup> with high FE (ca. 90%), but CO demands, on average, considerably lower overpotentials. In contrast, electrokinetics over reported methanol-producing systems occur efficiently (i.e., typical overpotentials of around 0.3 V), although with modest FE. Lastly,  $CH_4$  and  $C_2H_4$  typically demand overpotentials of ~1 V with scattered efficiency. Consequently, considerable differences in terms of energetic efficiency can be ascribed to different products in the current state of the art. It is important to note that mapped performances are not solely determined by electrokinetics because the calculated overpotentials for constructing Figure 1 are, in general, larger than those actually found on the catalytic surface as a consequence of polarization losses determined, among other factors (vide infra), by the design of the electrolytic cell. Such deviation can be expected to be modest at overpotentials below  $\sim 1 \text{ V.}^9$  In this sense, this analysis must be located in a previous stage to the electrokinetic evaluation of systems, where performance is driven solely by kinetics. A parallel analysis focused on electrode activity can be built based on the widely reported geometric partial current density. However, this analysis would not allow reliable comparisons across different systems, given the large influence of the catalyst loading, deposition method, roughness, etc., on



**Figure 1.** Performance map for the electrochemical reduction of  $CO_2$  (eCO<sub>2</sub>RR) toward the most commonly reported products. The maximum FE and its corresponding overpotential are plotted for each reported catalyst. The background color intensity is positively correlated to the density of points, suggesting characteristic values of FE–overpotentials for different products. They were obtained by KDE after establishing cutoff densities. Please note that the robustness of statistical analysis increases with the population size. Bibliographic references and relevant data for each report are provided in a separate Excel file and indexed in Figure S1.

the relationship between the geometric and electrochemically active surface areas.

Classification of Materials and Optimization Strategies. After establishing the typical performance regions for each product, we aimed to explore the relationship between different approaches to catalyst design and the resulting performance. To this end, we found that each reported eCO<sub>2</sub>RR system (i.e., the data points in Figure 1) could be classified into six basic families of materials and nine classes of optimization strategies (Figure 2). Because the presence of metals is almost universally required for the eCO<sub>2</sub>RR to occur to a significant extent (with a few exceptions, e.g., nitrogen-doped carbon materials), the materials are classified according to the architecture surrounding the metal atom(s), thus reflecting not only the different chemical identities of the catalysts but also the existence of different types of active sites. On the other hand, optimization strategies aim to tune properties relevant to the mechanism and/or thermodynamics of the reaction and can be classified in three distinct groups: strategies in a first group aim to modify surface adsorption properties by ligand effects, those in a second group achieve the stabilization of intermediates from the electrolyte, and a third group of approaches aim to optimize the performance by modifying the electrical and chemical environment within the double layer. In what follows, the material classes are described first, followed by the strategies.

Transition Metals. The  $eCO_2RR$  performance of transition metal electrodes has been rationalized by the relationship between the binding energies of reaction intermediates. For instance, the ability of Cu to produce highly reduced products in significant amounts is a consequence of the balance of its CO binding energy and its capacity to protonate adsorbed CO (to either \*COH or \*CHO) compared to other transition metals,

#### Perspective



**Figure 2.** Description of different classes of materials and optimization strategies as selectable parameters for the construction of  $eCO_2RR$  catalysts. Materials families are classified according to the different architecture of active sites, whereas optimization strategies refer to modifications of either relevant surface properties and/or the surrounding electrochemical environment. The images representing enzymes, chalcogenides, the chemical environment and electric field, co-catalysts, and functionalization are reprinted with permission from refs 11, 29, 58, 49, and 50, respectively. Copyright 2013, 2016, 2016, 2016, and 2017 American Chemical Society. The image representing surface strain is reprinted with permission from ref 42. Copyright 2017 John Wiley & Sons.

which either bind CO too weakly (leading to high selectivity toward CO, e.g., Au and Ag) or too strongly (resulting in poisoning by CO, e.g., Pt, Rh, Pd, and Ni).<sup>10</sup> However, theoretical studies indicate that the scaling relation between the binding energies of the CO\* and COOH\* intermediates in transition metal surfaces misses the top of the activity volcano for CO evolution.<sup>11</sup> In addition, the production rate of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> has been shown to have different sensitivity to pH and structure (e.g., Cu(111) and Cu(100) surfaces favor CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, respectively),<sup>12,13</sup> leading to the crucial mechanistic conclusion that these products follow independent pathways.<sup>14</sup>

p-Block Metals and Oxides. In contrast to transition metals, formate is the traditional  $eCO_2RR$  product over bulk p-block metals (e.g., Pb, In, Sn, Bi). The production of formate is thought to occur via a dead-end mechanism, which is different from that of CO, involving a weakly adsorbed  $CO_2^-$  radical or physisorbed  $CO_2$ .<sup>14,15</sup> Consequently, the high selectivity of p-block elements toward HCOO<sup>-</sup> is driven by the dominance of this alternative mechanism alongside poor HER kinetics. A distinctive feature of this materials family is that surface (hydr)oxides that are metastable under reducing conditions

appear to play a crucial role in the  $e{\rm CO}_2 RR$ , as revealed by in situ and operando experiments.  $^{16,17}$ 

Carbon-Based Materials. The performance of pure carbonbased materials in the  $eCO_2RR$  is generally low.<sup>18</sup> However, the introduction of nitrogen heteroatoms into the structure of carbon nanotubes  $(CNTs)^{19}$  and nanofibers  $(CNFs)^{20}$  has been shown to be successful in producing  $eCO_2RR$ -active metal-free catalysts. In general, the activity of these materials is thought to depend on the enhanced stabilization of reaction intermediates on either graphitic or pyridinic N sites.<sup>21</sup> More recently, the incorporation of isolated Fe atoms in N-doped carbon materials has resulted in enhanced performance.<sup>22</sup>

Molecular Catalysts. Broadly speaking, homogeneous catalysts for the  $eCO_2RR$  generally consist of transition metal complexes with (a) macrocyclic ligands (i.e., porphyrins, phthalocyanins, and cyclams), (b) bipyridine ligands, or (c) phospine ligands.<sup>23,24</sup> In light of concerns associated with the use of homogeneous catalysts, an emerging strategy is their immobilization over inert, conductive substrates. This approach has been recently demonstrated with promising results in the case of cobalt porphyrins,<sup>25</sup> for example, in which the electron



**Figure 3.** Performance maps of materials and optimization strategies reported for CO (top) and HCOO<sup>-</sup> (bottom). Maps associate the catalytic performance to materials (left) and optimization strategies (right). When one system integrates more than one optimization strategy, squares with different size overlap. The background color intensity is positively associated with the density of points, suggesting characteristic values of FE– overpotentials for different products. They were obtained from cluster analysis without imposition of cutoff densities. Bibliographic references and relevant data for each report are provided in a separate Excel file and indexed in Figure S1.

transfer to  $CO_2$  is thought to be mediated by the  $Co^{2+}/Co^+$  redox couple.<sup>26</sup>

Chalcogenides. Mo-terminated edge sites in  $MoS_2$  have been found to be active for the  $eCO_2RR_2^{27}$  and this observation has been recently extended to other transition metal dichalcogenides (TMDCs) with an engineered nanostructure. The high activity of the edge sites has been attributed to their low work function and high electronic density, particularly in WSe<sub>2</sub>.<sup>28</sup> Interestingly, DFT studies indicate that transition metal-doped  $MoS_2$  is able to break the scaling relation between  $eCO_2RR$ intermediates,<sup>29</sup> which encourages further development of this class of materials.

Enzymes. Although their use in practical contexts is very challenging, enzymes remain the only reported reversible electrocatalysts for  $\rm CO_2$  reduction to  $\rm CO^{30}$  and formate<sup>31</sup> (with the exception of some Pd-based materials in the case of the latter, vide infra), which makes them very valuable as benchmarks and for drawing inspiration for catalyst design. For instance, CO dehydrogenases contain bifunctional sites that avoid linear relationships present on transition metals and thus land on top of the activity volcano for CO evolution.<sup>11</sup>

Nanostructuring. Confining the size of the catalyst to the nanoscale is a common way to increase the population of exposed undercoordinated sites and thus achieve different adsorption properties with respect to bulk materials.<sup>32</sup> For instance, Pd nanoparticles below 5 nm show very high FE for CO (in stark contrast to bulk Pd), which was ascribed to an increased amount of corner and edge sites (with favorable CO<sub>2</sub> adsorption and \*COOH formation) relative to terrace sites, which are HER-active.<sup>33</sup> Another approach is to favor the exposure of crystallographic features with particular catalytic properties, as demonstrated by the increased production of ethylene over Cu mesocubes with a high density of (100) facets and atomic steps.<sup>34</sup>

Alloying. The adsorption properties of a metal can be tuned by changing the composition of the bulk or by limiting this alteration to the topmost and/or subsurface atomic layers (i.e., near-surface alloying).<sup>35</sup> An early experimental example is the finding by Sakata et al. of marked differences of selectivity over electrodeposited Cu-based alloys with d- and p-block metals.<sup>36</sup> DFT calculations have predicted alloys with enhanced

#### The Journal of Physical Chemistry Letters

performance toward different products, such as  $W-Au^{37}$  or  $Cu_3Pd^{38}$  for methanol.

Doping. Herein we expand the IUPAC definition of doping<sup>39</sup> to incorporate lattice substitution. The addition of dopants has been primarily used to improve the electrical conductivity of substrates, as in the case of boron-doped diamond.<sup>40</sup> On the contrary, lattice incorporation of nitrogen atoms in carbon materials has been revealed as a powerful tool to outfit carbon materials with unexpected eCO<sub>2</sub>RR properties (vide supra).

Surface Strain. The existence of tensile or compression strain in the lattice of a metal causes an upshift or a downshift of the d-band center, respectively. Because the d-band center is associated with adsorption strength, tensile strain results in stronger adsorbate binding, and vice versa.<sup>35</sup> Some systems, such as Au–Pd–Cu sandwich-like catalysts<sup>41</sup> or Pd nanoicosahedra,<sup>42</sup> show how this principle can be exploited to tune the FE.

Multiphase Systems. The interaction of different phases in multicomponent catalysts (e.g., supported nanoparticles) can result in interfacial sites with modified adsorption properties or in electronic effects on the active phase.<sup>43</sup> For example, studies of support effects are infrequent in the eCO<sub>2</sub>RR literature compared to (thermally-driven) heterogeneous catalysis, although the increase of the performance of Ag nanoparticles toward CO evolution when supported on TiO<sub>2</sub><sup>44</sup> or In(OH)<sub>3</sub><sup>45</sup> demonstrates the potential of this approach. In addition, metal–oxide interactions were reported to be crucial to the performance of Cu–In<sup>46</sup> and Au–CeO<sub>x</sub> electrocatalysts.<sup>47</sup>

Co-catalysts. Following the report of Rosen et al. that the presence of EMIM-BF<sub>4</sub> drastically reduces the onset potential for CO<sub>2</sub> reduction over Ag electrodes,<sup>7</sup> room-temperature ionic liquids (RTILs) have been commonly used as co-catalysts in the eCO<sub>2</sub>RR over different materials. They are believed to lower the energy of the  $CO_2^-$  intermediate, most likely by complexation, although there is still a lack of general consensus regarding the mechanism of action of RTILs in the eCO<sub>2</sub>RR.<sup>48,49</sup>

Functionalization. Molecules anchored to the catalyst surface may stabilize intermediates either by direct interaction with such species or by the redistribution of charges on the surface.<sup>50</sup> Most efforts have focused so far on understanding the effect of adsorbed halides, which are claimed to alter the adsorption energy of CO due to charge transfer from the halide to the metallic surface.<sup>51,52</sup>

Modification of the Chemical Environment. Pioneering studies by Hori and co-workers already demonstrated the influence of different cations<sup>53</sup> and anions<sup>54</sup> in the electrolyte on the eCO<sub>2</sub>RR. This effect has been recently rationalized by the more favorable hydrolysis of larger alkali cations in proximity to the cathode, leading to a buffering effect that reduces the pH-induced depletion of CO<sub>2</sub> on the electrode surface.<sup>55</sup> Another approach that belongs to this category is increasing the concentration of CO<sub>2</sub> in the electrolyte either by operating at higher pressures or by substituting the aqueous electrolyte by a suitable organic solvent.<sup>56</sup>

Electric Field. High local concentrations of cations and CO<sub>2</sub> are linked to each other due to noncovalent interactions.<sup>57</sup> By manipulating the electrode geometry, it is possible to modify the electric field and influence the distribution of charged species within the double layer to favor the eCO<sub>2</sub>RR.<sup>58</sup> This approach has been recently demonstrated by Sargent and co-workers using sharp Au nanotips that generate a very high local electric field. The intense field induces a high concentration of

cations (and, thus,  $CO_2$ ) over the active surface, resulting in greatly improved FE and current density.<sup>59</sup>

Visualization of Design-Performance Trends in the eCO<sub>2</sub>RR. Application of the dual classification (material and optimization strategies) to the reports plotted in Figure 1 gives rise to maps that allow visualization of trends between the different design approaches and the resulting catalytic performance for each eCO<sub>2</sub>RR product, as well as the identification of outliers. This breakdown for CO and HCOO<sup>-</sup>, the two most commonly reported eCO<sub>2</sub>RR products, is presented in Figure 3. Similar analyses for other products are shown in Figure S2 ( $C_2H_4$  and CH<sub>4</sub>) and Figure S3 (alcohols). Transition metals (CO) and pblock/oxides (HCOO<sup>-</sup>) largely give shape to characteristic zones, which are at a distance of the best-performing systems (enzymes). A variety of materials show remarkably high performance for CO evolution; for example, carbon-based,<sup>2</sup> d-metal,<sup>7</sup> and p-block/oxide<sup>60</sup> materials offer >90% FE at  $\eta$  < 0.2 V. As for formate, the typical  $\eta \approx 1$  V agrees with the commonly held belief that high selectivity is achieved only at the expense of very high overpotentials for the HER and not by favorable eCO2RR kinetics. Nevertheless, Pd-based<sup>61,62</sup> and Co-based materials<sup>63</sup> (which, remarkably, are not part of the pblock) have recently brought overpotentials closer to practical figures. In contrast, methane and ethylene are reported almost exclusively on transition metal (more precisely, Cu-containing) surfaces (Figure S2).

### High-performance eCO<sub>2</sub>RR toward CO seems to be heavily dependent on the strategy.

Consider now the impact of optimization strategies (Figure 3, right). As described, a system targeting CO production should impede the parasitic HER and either preferentially stabilize \*COOH over \*CO or reduce the energy barrier toward  $CO_2^{-.14}$  Notably, strategies that target stabilization from the electrolytic medium (i.e., modification of the chemical environment, electric field, and co-catalysts) are the only ones present in the best-performing systems, but nanostructuring also shows clear potential at this stage. On the other hand, functionalization, surface strain, alloying, and multiphase systems strategies need further development to overcome comparatively poor performances. As previously mentioned, the reaction mechanism for HCOO<sup>-</sup> is believed to proceed independently from CO formation.<sup>14</sup> Not surprisingly, the analysis of associated strategies in Figure 3 depicts a different landscape than that for CO. The nanostructuring approach helped to transform materials reported in their bulk form to be inactive for formate formation into benchmark catalysts (Pd and Co) when combined with modification of the electrochemical environment.<sup>64</sup> However, we remark that, in contrast to CO, the use of co-catalysts does not seem to be an effective driver for formate production. Some strategies such as doping, surface strain, or local modification of the electric field are almost or totally absent from available reports. Among the fewer amount of reports for more complex products, some general conclusions can be extracted. For example, the combination of nanostructuring with the modification of the electrochemical environment over Cu surfaces clearly predominates for  $CH_4$  and  $C_2H_4$  (Figure S2), whereas modification of the electrochemical environment has been largely used to favor methanol-producing systems (Figure S3). In summary, high-



Figure 4. Tafel slopes (*b*) and exchange current densities  $(j_0)$  (ECSA-normalized) associated with Au-based catalysts with different optimization strategies<sup>59</sup> with respect to a polycrystalline gold electrode<sup>65</sup> (left). Plot of the energy efficiency vs overpotential, considering a perfect oxygen evolution anode (OER, right) for the Au-based systems.

performance  $eCO_2RR$  toward CO seems to be heavily dependent on the strategy, led by those tuning the electrochemical environment around the electrode, in contrast to the acute dependency on the material-strategy combination revealed by recent results for HCOO<sup>-</sup>. A less varied picture emerges for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, where the ubiquitous use of Cu greatly determines the performance and makes it challenging to compare the merits of different strategies.

From Catalyst Screening to Electrokinetic Evaluation. Comparisons based on practical and directly measurable parameters (e.g., electrode potential, FE, geometric current density), such as those found in the maps, are valuable for screening catalysts tested under different conditions and identifying promising design approaches, but they provide, in general, limited information for developing a fundamental understanding of catalytic performance. Consequently, the screening must give way to electrokinetic studies determining the catalyst's energetics and intrinsic activity for the target and side reactions. In this context, the Tafel slope (b) and the exchange current density  $(j_0)$  are electrokinetic parameters commonly employed. At a basic level, a low Tafel slope is indicative of an efficient "translation" of increases of the applied potential into higher reaction rates for a given product, making it a valuable parameter from both fundamental and practical points of view. Figure 4 (left) exemplifies how the Tafel slope of Au-based catalysts (highly active and selective toward CO evolution Figure S1), vis-à-vis a polycrystalline electrode,<sup>65</sup> decreases through nanostructuring (Au nanoparticles and rods) and even further by the combination of nanostructuring with electric field effects (Au nanotips).<sup>59</sup> Interestingly, the values of  $i_0$  in this case suggest that nanostructuring seems to negatively affect the intrinsic activity, possibly due to the creation of a lower density of active sites compared to that of the polycrystalline surface. Although the influence of side reactions can be assessed by comparing partial current densities for each at fixed overpotentials, for example, a more practical analysis follows from the use of the energy efficiency (eq 1). Figure 4 (right) displays the superior behavior of both the polycrystalline electrode and the nanotips in achieving high energy efficiency toward CO.

It is important to note that such an analysis requires that (a) the experimental data be devoid of mass transfer limitations and (b) current densities be expressed in terms of the electro-

chemical surface area (ECSA) of the active phase. The former is challenging in the  $eCO_2RR$  due to the low concentration of  $CO_2$  in aqueous electrolytes and the multiproduct nature of the reaction, particularly in the case of products that are only observed at relatively high overpotentials with limited selectivity (e.g.,  $CH_4$  and  $C_2H_4$ ; see Figure 1).<sup>9</sup> In addition, accurate methods to determine the ECSA are currently available only for a limited group of materials, most of them noble metals.<sup>66,67</sup> As a consequence, electrokinetic characterizations will become more widely used in the  $eCO_2RR$  as novel catalysts exhibiting high FE at low overpotentials and new protocols for the determination of the ECSA are developed.

Development of Performance Descriptors. Looking ahead, the performance maps intend to encourage the "mix and match" design of eCO2RR catalysts, relying on the combination of effects from different building blocks. For instance, the electric field effect could be used to selectively increase the CO<sub>2</sub> local concentration next to surfaces with a high population of active sites, generated either by the creation of interfaces or by nanostructuring. Such systems would show reduced polarization losses and therefore reduced effective overpotentials. Another possibility could arise from using nanostructuring to create specific sites as targets for subsequent dopant substitution, facilitating atomically engineered doped materials. Nevertheless, a more rational optimization of eCO<sub>2</sub>RR electrocatalysts requires the development of new performance-driving parameters (i.e., descriptors) arising from mechanistic understanding. However, due to the current limitations of theoretical studies (e.g., simplification of the electrochemical interface), the development of performance descriptors demands complementary experimental efforts capable of (i) monitoring catalytically relevant properties (e.g., oxidation state, surface composition, and structure) under reaction conditions and/or (ii) developing model electrocatalytic systems where clear structure-performance relationships can be inferred. In this respect, although less accessible than in (thermally driven) heterogeneous catalysis due to their associated experimental complexity, spectroscopic operando techniques are increasingly applied to electrochemical reactions.<sup>68</sup> For instance, monitoring of surface species can be achieved by attenuated total reflectance infrared spectroscopy (ATR-IR)<sup>69,70</sup> or Raman spectroscopy.<sup>17</sup> The composition and

#### The Journal of Physical Chemistry Letters

oxidation state of the surface can be probed by synchrotronbased ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). X-ray absorption spectroscopy (XAS) does not require ultrahigh vacuum at the detector, and hard or soft X-rays can be used to probe metal catalyst atoms and adsorbed intermediate species, although its bulk character limits its applicability for nanostructured systems.<sup>71,72</sup> Last but not least, commercially available in situ electrochemical microscopy offers a promising avenue to disclose dynamic processes under reaction conditions over both flat and nanoparticulated materials. In addition, model catalysts intend to fill the gap between DFT models and real catalysts by precise control of the number and types of sites exposed. Model eCO2RR catalysts are even less frequent than in situ studies and are almost exclusively limited to nanoparticles with well-controlled morphologies.42,73 Nevertheless, atomically controlled Co oxide nanosheets<sup>63</sup> and nanofabricated doped diamond rods74 unveiled experimental descriptors allowing performance optimization studies, for example. Overall, we anticipate that theoretical efforts complemented by the clever use of operando techniques and model systems will drive future developments toward more efficient CO<sub>2</sub> reduction electrocatalysts.

> We anticipate that theoretical efforts complemented by the clever use of operando techniques and model systems will drive future developments toward more efficient CO<sub>2</sub> reduction electrocatalysts.

Performance Limitations and Metrics in  $CO_2$  (Photo)electrolyzers. In the second part of the Perspective, we shift the focus toward the development of practical devices for  $CO_2$ reduction. The optimization of  $CO_2$  electrolyzers demands the minimization of inefficiencies arising from a network of phenomena (kinetics, mass, and charge transport) of different nature, acting at different scales and, in general, not ascribed to a single component. This section briefly describes design parameters affecting the performance of the cathodic process because the anodic oxygen evolution<sup>75</sup> has been more profusely studied. Mathematical treatment of the optimization problem is out of the scope of this work. For models of (photo)electrochemical devices, the reader is referred to other sources.<sup>9,76,77</sup>

The performance of an electrolyzer can be quantified in terms of the energy efficiency and the product formation rate. Thus, design—performance optimization can be mathematically modeled and performance limitations quantified (scheme in Figure 4). The energy efficiency in electrolyzers ( $\varepsilon_e$ , also known as voltage efficiency) is defined as the ratio between the chemical energy stored in the desired product(s) *i* and the applied electrical energy and can be calculated with eq 1. The additional cell voltage over the equilibrium potential (i.e., the thermoneutral value,  $E^n$ ) is the sum of cathodic and anodic overvoltages arising from kinetics (kinetic overpotential,  $\eta^{\text{act}}$ ), charge transport (ohmic overpotential,  $\eta^{\text{ohm}}$ ), and mass transport (diffusion overpotential,  $\eta^{\text{mt}}$ ). A detailed mathematical description of these variables can be found in a number of works.<sup>9,75</sup> The partial current density of the desired product *i* 

 $(j_i)$  is a fraction of the total current density given by the FE  $S_i$  (eq 2).

$$\varepsilon_{\rm e}(j) = \sum_{i} \frac{E_i^n \cdot S_i}{E_i^n + \eta^{\rm act} + \eta^{\rm ohm} + \eta^{\rm mt}} = \sum_{i} \frac{E_i^n \cdot S_i}{E_{\rm cell}}$$
(1)

$$j_i = S_i \cdot j(E_{\text{cell}}) \tag{2}$$

Design- and performance-limiting parameters are linked in  $CO_2$  electrolyzers (scheme in Figure 4). Particular aspects associated with photoelectrochemical cells are described later.

Thermodynamic Limitation. Thermodynamics imposes a minimum cell voltage equal to  $E^n$  (Table S1).<sup>2</sup> The thermodynamic limitation in this context refers to a positive shift of  $E^n$  under operation as a consequence of  $CO_2$  depletion and/or raised pH at the catalytic surface (Nernstian loss). In CO2-bubbling electrolyzers, both processes are linked by carbonate equilibria and reaction stoichiometry. Shifts in  $E^n$ are therefore driven by (i) the buffer capacity of the electrolyte<sup>78</sup> and the solubility of  $CO_2$  (and its kinetics)<sup>9</sup> and (ii) the thickness of the diffusion layer, directly associated with the degree of turbulence and therefore to the cell design. Singh et al.9 estimated shifts of 100 and 50 mV associated with pH and CO<sub>2</sub> local variations, respectively (15 mA cm<sup>-2</sup>, diffusion layer thickness of 100  $\mu$ m). They can thus become comparable to kinetic overpotentials over state-of-the-art catalysts (Figure 1). Remarkably, the configuration based on a gas diffusion electrode (GDE) avoids CO<sub>2</sub> depletion and provokes turbulent flow at the catalytic surface, therefore minimizing the impact of this limitation.

Kinetic Limitation. The kinetic overpotential  $\eta^{\rm act}$  and FE  $S_i$  arises from the energetic landscape of the reaction mechanism, which is determined by the electrocatalyst, the electrolyte, and, importantly, transport properties (cell design) in the case of pH-dependent reactions<sup>14</sup> and/or reaction products unstable under highly alkaline conditions.<sup>79</sup> The porous structure of the catalytic layer also plays a role as adsorption properties may change in nanometric pores when double layers overlap (nanoconfinement effect).<sup>80</sup> The cathodic overpotential is currently the largest source of inefficiencies in well-designed electrolyzers, accounting for 400–800 mV at 10–50 mA cm<sup>-2,81</sup> followed by the anodic one (200–300 mV at similar current densities).<sup>75</sup>

Transport Limitation. Charge and mass transport limitations are manifested in the Joule effect and concentration gradients, respectively. Out of the ionic and electronic contributions to the ohmic losses through the Joule effect, the ionic one introduced by the electrolyte is predominant (stainless steel<sup>82</sup>  $\approx 1.4 \times 10^{-6}$  S m<sup>-1</sup> vs 0.1 M KHCO<sub>3</sub> electrolyte<sup>83</sup>  $\approx 7$  S m<sup>-1</sup>), which calls for a short distance between electrodes for high performance. Though the ohmic overpotential  $\eta^{ohm}$  can be thus decreased by increasing the conductivity of the electrolyte, this beneficial effect is largely counterbalanced by an increase of the thermoneutral potential as a consequence of larger concentration gradients arising from a weaker electric field. The net effect is estimated to correspond to  $\sim$ 3.5 mV S<sup>-1</sup> according to Singh et al.9 They also modeled the key impact of the membrane ion selectivity on the electric field. Electrodialysis forced by the use of cationic membranes brings large polarization losses (ca. 300 mV at 4 mA cm<sup>-2</sup>). Consequently, ohmic overpotentials can be minimized by proper selection of the electrolyte, membrane, and geometry but can become the main limitation in other cases, as reported by Kopjlar et al.,<sup>84</sup>



**Figure 5.** (Top) Scheme showing the interconnection of design and performance limitations using a color code. (a) Calculation of the points  $j_{\varepsilon}$  (associated with the maximum energy efficiency) and  $\varepsilon_j$  (associated with the maximum product formation rate) from the characteristic electrochemical curve (dashed red) and energy efficiency evolution (solid black) of a hypothetical electrolyzer with a real cathode and idealized anode (see text). (b) Determination of the operation point for an artificial leaf formed by system (a) coupled to a real photoabsorber (solid orange). (c) Representation of the performance metrics extracted from (a) and (b). (d) Comparison of performance metrics ( $\varepsilon_j$   $j_{\varepsilon}$ ) for reported electrolyzers yielding different carbon products. The shadowed area comprises achievable solar-to-fuel efficiencies and current densities for artificial leaves (see the Excel file in the Supporting Information for references). Typical performance for a water splitting device<sup>75</sup> is added as "H<sub>2</sub>".

where  $\eta^{\text{ohm}} \approx 950 \text{ mV}$  at 100 mA cm<sup>-2</sup>. In parallel, mass transport properties have a decisive influence in thermodynamic, kinetic, and ohmic losses. Ionic gradients in the boundary layer next to the electrode give rise to diffusion losses, represented by  $\eta^{\text{mt}}$  and usually modeled using unidimensional Fick's law.<sup>85</sup> For the CO<sub>2</sub>-bubbling configuration at ambient conditions, the limiting current density  $j_i$  is strongly dependent on the electrolyte pH, conductivity, hydrodynamics, and number of CO<sub>2</sub> moles consumed per mole of electrons transferred. Local effects such as complex diffusion patterns at nanostructured surfaces and electric field effects are usually disregarded, despite their influence on the  $CO_2$  concentration near the electrode.<sup>59</sup> However,  $j_i$  is restricted<sup>9</sup> to tens of mA cm<sup>-2</sup> in any case, which renders this configuration as unsuitable for industrial standards. On the other hand, electrolyzers based on GDEs are only limited in this respect by the ionic flux through the catalytic layer. In this situation, microscopic models predict<sup>86</sup> confinement of the catalytic activity into a small fraction of the catalyst layer at high current densities, characterized by the appearance of a virtual kinetic overvoltage  $\eta^{mt} = \eta^{act}$ .

Finally, note that the overvoltages described show different evolutions as the current density increases. Consequently, performance limitations vary in their importance according to operation conditions.<sup>2</sup> All in all, the anticipated picture of a multivariable optimization problem emerges and calls for an integral engineering approach in order to achieve the primary goal of high efficiency.

Quantifying the Performance Gap toward Practical Implementation. An aspect highlighted often is the need for figures of merit (based on technoeconomic analyses) to guide the development of electrolyzers toward practical implementation.<sup>2,87</sup> In this context, herein we introduce simple and robust performance metrics, derived from the conventional cell voltage-FE-current density trio, that (a) facilitate the comparison among systems at practically relevant operation conditions and (b) provide a first quantitative approach to how energy efficiency evolves as the product formation rate increases. In this regard, we note that the nominal working regime in a practical device must be located between the conditions that maximize the product formation rate per unit of energy input and those that maximize the total product formation rate (associated with high and low electricity cost scenarios, respectively). Operation outside of this range would make little pecuniary sense. These two maxima in general do not overlap because electrokinetics demand higher overpotentials (i.e., lower energy efficiency) for increasingly larger current densities. To this end, we consider the partial current density of the desired product obtained at maximum energy efficiency  $(i_{\epsilon})$  and the energy efficiency obtained at maximum partial current density  $(\varepsilon_i)$ . The calculation of the pair  $(\varepsilon_i, j_e)$  is exemplified in Figure 5a for a cell producing CO (kinetic data obtained from Hatsukade et al.<sup>88</sup>) alongside an idealized  $IrO_2$ anode (Tafel equation, cathodic transfer coefficient  $\alpha_c = 1$ , exchange current density  $j_0 = 1.4 \times 10^{-4}$  mA cm<sup>-2</sup>). The pair is represented in Figure 5b. The slope of the segment linking these two points represents the decay rate of energy efficiency as the production rate increases (thus, a horizontal line would correspond to the ideal thermodynamic behavior), and its horizontal length reflects the operation range. Note that  $j_{\epsilon}$ mainly encompasses kinetic limitations, whereas  $\varepsilon_i$  displays a larger influence of transport limitations, that is, is more influenced by engineering aspects. Comparison among systems is thus straightforward. For example, some representative reports are compared in Figure 5d (references can be found in an Excel file in the Supporting Information). CO and HCOO<sup>-</sup> electrolyzers lead the feasibility race (see also Figure 1) though still at modest  $\varepsilon_i$  values in comparison to expected practical ones.<sup>2</sup> As an example, Kenis et al.<sup>89</sup> (label a) and Dufek et al.<sup>90</sup> (label b) reported similar  $j_{\varepsilon}$  for CO production using Ag-based eCO<sub>2</sub>RR catalysts. However, careful engineering in conjunction with a state-of-art anode translated into a decay of 0.12% per unit of current density ("a"), vs. 1.04% for "b". For the sake of comparison, an average performance for a state-of-the-art polymeric membrane water electrolyzer (a technology entering industrial implementation) is shown in Figure 5d ("H<sub>2</sub>"). The lack of side reactions and a very kinetically efficient hydrogen production in the cathode, together with decades of engineering efforts,<sup>75</sup> result in elevated energy efficiencies over a very wide range of current densities (decay rate ~0.01%). Nevertheless, technical similarities between water splitting and electrochemical CO<sub>2</sub> reduction hint at the potential of combining catalyst design and device engineering in CO<sub>2</sub> electrolyzers.

Photoelectrochemical Cells (PECs). All previous considerations on limiting phenomena can be directly translated to  $CO_2$ reducing PECs. However, the direct transformation of sunlight into photovoltage suffers from both extrinsic and intrinsic losses (scheme in Figure 5). Extrinsic losses such as nonradiative recombination, series resistance, or reflection can be minimized by proper cell design. On the other hand, intrinsic ones (mismatch between the solar spectrum and energy band gap and radiative recombination) are inherent to light absorbers. As a result, the maximum current density for  $CO_2$  reduction under solar light is around 35 mA cm<sup>-2</sup> even under ideal conditions and optimum configuration of light absorbers.<sup>76</sup> This key outcome (a) minimizes the impact of limiting phenomena associated with high current densities (ohmic losses and poor mass transport), (b) makes the  $CO_2$ -bubbling configuration a suitable design option, and (c) facilitates catalyst design as requirements on specific electroactive surface area are milder.

Operation in PECs is defined by crossing of the voltage– current characteristics of the light absorber(s) and the electrocatalytic system.<sup>91</sup> In Figure 5b, the same system described in Figure 5a is coupled to a high-performance triple-junction InGaP/GaS/Ge absorber under AMG 1.5.<sup>76</sup> The resulting operation point is located far from both the optimal operation range determined by ( $\varepsilon_j$ ,  $j_{\varepsilon}$ ) and the one corresponding to optimal photoconversion, yielding a solarto-fuel efficiency of  $\varepsilon_{stf} = 1.33\%$  (Figure 5c). It follows that coupling high-performance eCO<sub>2</sub>RR systems and photoabsorbers does not necessarily lead to a high-performance artificial leaf. An integral design approach among different disciplines, focused on matching energy band gaps and kinetic overpotentials with dedicated interface engineering, is thus prerequisite.<sup>92</sup> In this respect, examples of current efforts are the Joint Centre for Artificial Photosynthesis in the United States<sup>93</sup> or the a-leaf project funded by the European Union.<sup>94</sup>

Because PECs are characterized by a nominal operation point (assuming constant irradiation),  $\varepsilon_j = j_e$  follows. Bell et al.<sup>76</sup> have calculated thermodynamic and real performances of artificial leaves, arriving at ideal  $\varepsilon_{\rm stf} = 30-35\%$  for almost all carbon products except for CO (42%); see Figure 5d (shadowed area). Replacement of perfect kinetics by a state-of-the-art Ag eCO<sub>2</sub>RR catalyst would decrease  $\varepsilon_{\rm stf}$  down to 7%. Lastly, when state-of-the-art catalysts and absorbers are considered, efficiencies around 1% must be expected. These figures are in stark contrast with those expected in electrolyzers coupled to other renewable sources such as hydro or wind, with larger electrical conversion efficiency (up to 90 and 45%, respectively).

Conclusions and Outlook. The electrokinetics of  $CO_2$ reduction remains as the main source of inefficiency in electrolyzers. This is in part explained by the scarcity of design-performance relationships driving the rational design and optimization of catalysts. Materials- and optimization strategy-performance maps suggest patterns for different products and offer a bird's eye of the field, where electrocatalysis toward CO and HCOO<sup>-</sup> shows promising selectivity and overpotentials. In conjunction with electrokinetics, mass and charge transport properties profile operation at the device level, which makes an integral design from the active site to the cell scale prerequisite toward high performance. In contrast, a careful match of electrokinetics and photoconversion characteristics is the key design step in photoelectrochemical cells. Finally, simple and robust metrics for performance based on maximum energy efficiency and product formation rate shows how improvement is needed on both electrocatalysis and engineering before meeting practical requirements.

At the device level, analysis of the network of limiting phenomena in (photo)electrochemical cells leads us to propose a straightforward performance metric based on the concepts of maximum energy efficiency and maximum product formation rate, enabling the comparison of different technologies.

We put forward that experimental in situ techniques and model systems will complement theoretical efforts on unveiling performance descriptors in coming years, gradually shifting from the traditional trial and error approach to a more rational design of catalysts. As a consequence, we expect to see a parallel and quick rise in engineering efforts as industrial feasibility is perceived as a midterm goal, which must benefit from the wake of similar and more developed technologies such as water splitting. In light of the herein presented results and recent feasibility studies, we highlight the potential of formate as the first product to break the commercialization barrier. The recently reported development of electrocatalytic systems at the lab scale that combine low overpotentials with high selectivity may boost the process as long as similar performance can be replicated on inexpensive and scalable materials.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01380.

Thermodynamic data of  $CO_2$  reduction reactions, performance map of the  $eCO_2RR$  with indices for each report, and performance maps for materials and optimization strategies for hydrocarbons and alcohols (PDF)

Bibliographic references and relevant data for construction of the performance maps (XLSX)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: jpr@chem.ethz.ch. Phone: +41 44 633 7120.

#### ORCID 0

Javier Pérez-Ramírez: 0000-0002-5805-7355

#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was sponsored by ETH Zurich (Research Grant ETH-01 14-1) and by the European Union under the a-leaf project (732840-A-LEAF).

#### REFERENCES

(1) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazábal, G. O.; Pérez-Ramírez, J. Status and Perspectives of  $CO_2$  Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes. *Energy Environ. Sci.* **2013**, *6*, 3112–3135.

(2) Martín, A. J.; Larrazábal, G. O.; Pérez-Ramírez, J. Towards Sustainable Fuels and Chemicals through the Electrochemical Reduction of  $CO_2$ : Lessons from Water Electrolysis. *Green Chem.* **2015**, 17, 5114–5130.

(3) Hori, Y.; Kikuchi, K.; Suzuki, S. Production of CO and  $CH_4$  in Electrochemical Reduction of  $CO_2$  at Metal Electrodes in Aqueous Hydrogencarbonate Solution. *Chem. Lett.* **1985**, *14*, 1695–1698.

(4) Azuma, M.; Hashimoto, K.; Watanabe, M. Electrochemical Reduction of Carbon Dioxide on Various Metal Electrodes in Low-Temperature Aqueous KHCO<sub>3</sub> Media. *J. Electrochem. Soc.* **1990**, *137*, 1772–1778.

(5) Mistry, H.; Reske, R.; Zeng, Z.; Zhao, Z.; Strasser, P.; Cuenya, B. R.; Greeley, J. Exceptional Size-Dependent Activity Enhancement in the Electroreduction of  $CO_2$  over Au Nanoparticles. J. Am. Chem. Soc. **2014**, 136, 16473–16476.

(6) Salehi-Khojin, A.; Jhong, H. R. M.; Rosen, B. A.; Zhu, W.; Ma, S.; Kenis, P. J. A.; Masel, R. I. Nanoparticle Silver Catalysts That Show Enhanced Activity for Carbon Dioxide Electrolysis. *J. Phys. Chem. C* **2013**, *117*, 1627–1632.

(7) Rosen, B. A.; Salehi-Khojin, A.; Thorson, M. R.; Zhu, W.; Whipple, D. T.; Kenis, P. J. A.; Masel, R. I. Ionic Liquid–Mediated Selective Conversion of  $CO_2$  to CO at Low Overpotentials. *Science* **2011**, 334, 643–644.

(8) Verma, S.; Kim, B.; Jhong, H. R. M.; Ma, S.; Kenis, P. J. A. A Gross-Margin Model for Defining Technoeconomic Benchmarks in the Electroreduction of CO<sub>2</sub>. *ChemSusChem* **2016**, *9*, 1972–1979.

(9) Singh, M. R.; Clark, E. L.; Bell, A. T. Effects of Electrolyte, Catalyst, and Membrane Composition and Operating Conditions on the Performance of Solar-Driven Electrochemical Reduction of Carbon Dioxide. *Phys. Chem. Chem. Phys.* **2015**, *17*, 18924–18936.

(10) Peterson, A. A.; Nørskov, J. K. Activity Descriptors for  $CO_2$ Electroreduction to Methane on Transition-Metal Catalysts. *J. Phys. Chem. Lett.* **2012**, 3, 251–258.

(11) Hansen, H. A.; Varley, J. B.; Peterson, A. A.; Norskov, J. K. Understanding Trends in the Electrocatalytic Activity of Metals and Enzymes for  $CO_2$  Reduction to CO. J. Phys. Chem. Lett. **2013**, 4, 388–392.

(12) Hori, Y.; Takahashi, R.; Yoshinami, Y.; Murata, A. Electrochemical Reduction of CO at a Copper Electrode. *J. Phys. Chem. B* **1997**, *101*, 7075–7081.

(13) Hori, Y.; Takahashi, I.; Koga, O.; Hoshi, N. Selective Formation of C2 Compounds from Electrochemical Reduction of CO<sub>2</sub> at a Series of Copper Single Crystal Electrodes. *J. Phys. Chem. B* **2002**, *106*, 15–17.

(14) Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M. Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J. Phys. Chem. Lett.* **2015**, *6*, 4073–4082.

(15) Cheng, T.; Xiao, H.; Goddard, W. A. Reaction Mechanisms for the Electrochemical Reduction of  $CO_2$  to CO and Formate on the Cu(100) Surface at 298 K from Quantum Mechanics Free Energy Calculations with Explicit Water. *J. Am. Chem. Soc.* **2016**, *138*, 13802–13805.

(16) Pander, J. E.; Baruch, M. F.; Bocarsly, A. B. Probing the Mechanism of Aqueous  $CO_2$  Reduction on Post-Transition-Metal Electrodes Using ATR-IR Spectroelectrochemistry. *ACS Catal.* **2016**, *6*, 7824–7833.

(17) Dutta, A.; Kuzume, A.; Rahaman, M.; Vesztergom, S.; Broekmann, P. Monitoring the Chemical State of Catalysts for  $CO_2$  Electroreduction: An In Operando Study. *ACS Catal.* **2015**, *5*, 7498–7502.

(18) Yang, N.; Waldvogel, S. R.; Jiang, X. Electrochemistry of Carbon Dioxide on Carbon Electrodes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 28357–28371.

#### The Journal of Physical Chemistry Letters

(20) Kumar, B.; Asadi, M.; Pisasale, D.; Sinha-Ray, S.; Rosen, B. A.; Haasch, R.; Abiade, J.; Yarin, A. L.; Salehi-Khojin, A. Renewable and Metal-Free Carbon Nanofibre Catalysts for Carbon Dioxide Reduction. *Nat. Commun.* **2013**, *4*, 2819.

(21) Sharma, P. P.; Wu, J.; Yadav, R. M.; Liu, M.; Wright, C. J.; Tiwary, C. S.; Yakobson, B. I.; Lou, J.; Ajayan, P. M.; Zhou, X. Nitrogen-Doped Carbon Nanotube Arrays for High-Efficiency Electrochemical Reduction of  $CO_2$ : On the Understanding of Defects, Defect Density, and Selectivity. *Angew. Chem., Int. Ed.* **2015**, *54*, 13701–13705.

(22) Huan, T. N.; Ranjbar, N.; Rousse, G.; Sougrati, M.; Zitolo, A.; Mougel, V.; Jaouen, F.; Fontecave, M. Electrochemical Reduction of CO  $_2$  Catalyzed by Fe-N-C Materials: A Structure–Selectivity Study. ACS Catal. 2017, 7, 1520–1525.

(23) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Electrocatalytic and Homogeneous Approaches to Conversion of  $CO_2$  to Liquid Fuels. *Chem. Soc. Rev.* **2009**, *38*, 89–99.

(24) Costentin, C.; Robert, M.; Savéant, J.-M. Catalysis of the Electrochemical Reduction of Carbon Dioxide. *Chem. Soc. Rev.* 2013, 42, 2423–2436.

(25) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M.; et al. Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic  $CO_2$  Reduction in Water. *Science* **2015**, *349*, 1208–1213.

(26) Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y. Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K. J. P.; Mul, G.; Koper, M. T. M. Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide and Methane at an Immobilized Cobalt Protoporphyrin. *Nat. Commun.* **2015**, *6*, 8177.

(27) Asadi, M.; Kumar, B.; Behranginia, A.; Rosen, B. A.; Baskin, A.; Repnin, N.; Pisasale, D.; Phillips, P.; Zhu, W.; Haasch, R.; et al. Robust Carbon Dioxide Reduction on Molybdenum Disulphide Edges. *Nat. Commun.* **2014**, *5*, 1456–1465.

(28) Asadi, M.; Kim, K.; Liu, C.; Addepalli, A. V.; Abbasi, P.; Yasaei, P.; Phillips, P.; Behranginia, A.; Cerrato, J. M.; Haasch, R.; et al. Nanostructured Transition Metal Dichalcogenide Electrocatalysts for CO2 Reduction in Ionic Liquid. *Science* **2016**, *353*, 467–470.

(29) Hong, X.; Chan, K.; Tsai, C.; Nørskov, J. K. How Doped  $MoS_2$ Breaks Transition-Metal Scaling Relations for  $CO_2$  Electrochemical Reduction. *ACS Catal.* **2016**, *6*, 4428–4437.

(30) Jeoung, J.-H.; Dobbek, H. Carbon Dioxide Activation at the Ni,Fe-Cluster of Anaerobic Carbon Monoxide Dehydrogenase. *Science* **2007**, *318*, 1461–1464.

(31) Bassegoda, A.; Madden, C.; Wakerley, D. W.; Reisner, E.; Hirst, J. Reversible Interconversion of  $CO_2$  and Formate by a Molybdenum-Containing Formate Dehydrogenase. *J. Am. Chem. Soc.* **2014**, *136*, 15473–15476.

(32) Bligaard, T.; Nørskov, J. K. Ligand Effects in Heterogeneous Catalysis and Electrochemistry. *Electrochim. Acta* 2007, *52*, 5512–5516.

(33) Gao, D.; Zhou, H.; Wang, J.; Miao, S.; Yang, F.; Wang, G.; Wang, J.; Bao, X. Size-Dependent Electrocatalytic Reduction of CO<sub>2</sub> over Pd Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 4288–4291.

(34) Chen, C. S.; Handoko, A. D.; Wan, J. H.; Ma, L.; Ren, D.; Yeo, B. S. Stable and Selective Electrochemical Reduction of Carbon Dioxide to Ethylene on Copper Mesocrystals. *Catal. Sci. Technol.* **2015**, *5*, 161–168.

(35) Bandarenka, A. S.; Koper, M. T. M. Structural and Electronic Effects in Heterogeneous Electrocatalysis: Toward a Rational Design of Electrocatalysts. *J. Catal.* **2013**, *308*, 11–24.

(36) Watanabe, M.; Shibata, M.; Katoh, A.; Sakata, T.; Azuma, M. Design of Alloy Electrocatalysts for CO<sub>2</sub> Reduction: Improved Energy Efficiency, Selectivity, and Reaction Rate for the CO<sub>2</sub> Electroreduction on Cu Alloy Electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, 305, 319–328.

(37) Back, S.; Kim, H.; Jung, Y. Selective Heterogeneous CO<sub>2</sub> Electroreduction to Methanol. *ACS Catal.* **2015**, *5*, 965–971.

(38) Hirunsit, P.; Soodsawang, W.; Limtrakul, J. CO<sub>2</sub> Electrochemical Reduction to Methane and Methanol on Copper-Based Alloys: Theoretical Insight. *J. Phys. Chem. C* **2015**, *119*, 8238–8249.

(39) Haber, J. Manual on Catalyst Characterization (Recommendations 1991). *Pure Appl. Chem.* **1991**, *63*, 1227–1246.

(40) Nakata, K.; Ozaki, T.; Terashima, C.; Fujishima, A.; Einaga, Y. High-Yield Electrochemical Production of Formaldehyde from CO<sub>2</sub> and Seawater. *Angew. Chem., Int. Ed.* **2014**, *53*, 871–874.

(41) Januszewska, A.; Jurczakowski, R.; Kulesza, P. J.  $CO_2$ Electroreduction at Bare and Cu-Decorated Pd Pseudomorphic Layers: Catalyst Tuning by Controlled and Indirect Supporting onto Au(111). *Langmuir* **2014**, *30*, 14314–14321.

(42) Huang, H.; Jia, H.; Liu, Z.; Gao, P.; Zhao, J.; Luo, Z.; Yang, J.; Zeng, J. Understanding of Strain Effects in the Electrochemical Reduction of CO<sub>2</sub>: Using Pd Nanostructures as an Ideal Platform. *Angew. Chem.* **2017**, *129*, 3648–3652.

(43) Hayden, B. E. Particle Size and Support Effects in Electrocatalysis. Acc. Chem. Res. 2013, 46, 1858–1866.

(44) Ma, S.; Lan, Y.; Perez, G. M. J.; Moniri, S.; Kenis, P. J. A. Silver Supported on Titania as an Active Catalyst for Electrochemical Carbon Dioxide Reduction. *ChemSusChem* **2014**, *7*, 866–874.

(45) Larrazábal, G. O.; Martín, A. J.; Mitchell, S.; Hauert, R.; Pérez-Ramírez, J. Synergistic Effects in Silver–indium Electrocatalysts for Carbon Dioxide Reduction. J. Catal. 2016, 343, 266–277.

(46) Larrazábal, G. O.; Martín, A. J.; Mitchell, S.; Hauert, R.; Pérez-Ramírez, J. Enhanced Reduction of  $CO_2$  to CO over Cu-In Electrocatalysts: Catalyst Evolution Is the Key. *ACS Catal.* **2016**, *6*, 6265–6274.

(47) Gao, D.; Zhang, Y.; Zhou, Z.; Cai, F.; Zhao, X.; Huang, W.; Li, Y.; Zhu, J.; Liu, P.; Yang, F.; et al. Enhancing CO<sub>2</sub> Electroreduction with the Metal-Oxide Interface. *J. Am. Chem. Soc.* **2017**, *139*, 5652–5655.

(48) Lim, H.-K.; Kim, H. The Mechanism of Room-Temperature Ionic-Liquid-Based Electrochemical  $CO_2$  Reduction: A Review. *Molecules* **2017**, *22*, 536.

(49) Lau, G. P. S.; Schreier, M.; Vasilyev, D.; Scopelliti, R.; Grätzel, M.; Dyson, P. J. New Insights Into the Role of Imidazolium-Based Promoters for the Electroreduction of  $CO_2$  on a Silver Electrode. *J. Am. Chem. Soc.* **2016**, *138*, 7820–7823.

(50) Fang, Y.; Flake, J. C. Electrochemical Reduction of  $CO_2$  at Functionalized Au Electrodes. J. Am. Chem. Soc. **2017**, 139, 3399–3405.

(51) Won, D. H.; Shin, H.; Koh, J.; Chung, J.; Lee, H. S.; Kim, H.; Woo, S. I. Highly Efficient, Selective, and Stable CO<sub>2</sub> Electroreduction on a Hexagonal Zn Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 9297–9300.

(52) Varela, A. S.; Ju, W.; Reier, T.; Strasser, P. Tuning the Catalytic Activity and Selectivity of Cu for  $CO_2$  Electroreduction in the Presence of Halides. *ACS Catal.* **2016**, *6*, 2136–2144.

(53) Murata, A.; Hori, Y. Product Selectivity Affected by Cationic Species in Electrochemical Reduction of  $CO_2$  and CO at a Cu Electrode. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 123–127.

(54) Hori, Y.; Murata, A.; Takahashi, R. Formation of Hydrocarbons in the Electrochemical Reduction of Carbon Dioxide at a Copper Electrode in Aqueous Solution. *J. Chem. Soc., Faraday Trans.* 1 1989, 85, 2309–2326.

(55) Singh, M. R.; Kwon, Y.; Lum, Y.; Ager, J. W.; Bell, A. T. Hydrolysis of Electrolyte Cations Enhances the Electrochemical Reduction of  $CO_2$  over Ag and Cu. J. Am. Chem. Soc. **2016**, 138, 13006–13012.

(56) Jitaru, M.; Lowy, D. A.; Toma, M.; Toma, B. C.; Oniciu, L. Electrochemical Reduction of Carbon Dioxide on Flat Metallic Cathodes. J. Appl. Electrochem. **1997**, *27*, 875–889.

(57) Varela, A. S.; Kroschel, M.; Reier, T.; Strasser, P. Controlling the Selectivity of  $CO_2$  Electroreduction on Copper: The Effect of the Electrolyte Concentration and the Importance of the Local pH. *Catal. Today* **2016**, *260*, 8–13.

(58) Chen, L. D.; Urushihara, M.; Chan, K.; Nørskov, J. K. Electric Field Effects in Electrochemical  $CO_2$  Reduction. *ACS Catal.* **2016**, *6*, 7133–7139.

(59) Liu, M.; Pang, Y.; Zhang, B.; De Luna, P.; Voznyy, O.; Xu, J.; Zheng, X.; Dinh, C. T.; Fan, F.; Cao, C.; et al. Enhanced Electrocatalytic CO<sub>2</sub> Reduction via Field-Induced Reagent Concentration. *Nature* **2016**, *537*, 382–386.

(60) DiMeglio, J. L.; Rosenthal, J. Selective Conversion of  $CO_2$  to CO with High Efficiency Using an Inexpensive Bismuth-Based Electrocatalyst. J. Am. Chem. Soc. **2013**, 135, 8798–8801.

(61) Kortlever, R.; Peters, I.; Koper, S.; Koper, M. T. M. Electrochemical  $CO_2$  Reduction to Formic Acid at Low Overpotential and with High Faradaic Efficiency on Carbon Supported Bimetallic Pd-Pt Nanoparticles. *ACS Catal.* **2015**, *5*, 3916–3923.

(62) Klinkova, A.; De Luna, P.; Dinh, C.-T.; Voznyy, O.; Larin, E. M.; Kumacheva, E.; Sargent, E. H. Rational Design of Efficient Palladium Catalysts for Electroreduction of Carbon Dioxide to Formate. *ACS Catal.* **2016**, *6*, 8115–8120.

(63) Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Li, D.; Yang, J.; Xie, Y. Partially Oxidized Atomic Cobalt Layers for Carbon Dioxide Electroreduction to Liquid Fuel. *Nature* **2016**, *529*, 68–71.

(64) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-Carbon Fuels. *Chem. Soc. Rev.* **2014**, *43*, 631–675.

(65) Wuttig, A.; Yaguchi, M.; Motobayashi, K.; Osawa, M.; Surendranath, Y. Inhibited Proton Transfer Enhances Au-Catalyzed CO<sub>2</sub>-to-Fuels Selectivity. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, E4585–93.

(66) Trasatti, S.; Petrii, O. A. Real Surface Area Measurements in Electrochemistry. *Pure Appl. Chem.* **1991**, *63*, 711–734.

(67) Łukaszewski, M.; Soszko, M.; Czerwiński, A. Electrochemical Methods of Real Surface Area Determination of Noble Metal Electrodes - an Overview. *Int. J. Electrochem. Sci.* **2016**, *11*, 4442–4469.

(68) Choi, Y.-W.; Mistry, H.; Roldan Cuenya, B. New Insights into Working Nanostructured Electrocatalysts through Operando Spectroscopy and Microscopy. *Curr. Opin. Electrochem.* **2017**, *1*, 95–103.

(69) Baruch, M. F.; Pander, J. E.; White, J. L.; Bocarsly, A. B. Mechanistic Insights into the Reduction of  $CO_2$  on Tin Electrodes Using in Situ ATR-IR Spectroscopy. ACS Catal. **2015**, *5*, 3148–3156.

(70) Firet, N. J.; Smith, W. A. Probing the Reaction Mechanism of CO<sub>2</sub> Electroreduction over Ag Films via Operando Infrared Spectroscopy. *ACS Catal.* **2017**, *7*, 606–612.

(71) Rosen, J.; Hutchings, G. S.; Lu, Q.; Forest, R. V.; Moore, A.; Jiao, F. Electrodeposited Zn Dendrites with Enhanced CO Selectivity for Electrocatalytic CO<sub>2</sub> Reduction. *ACS Catal.* **2015**, *5*, 4586–4591.

(72) Mistry, H.; Varela, A. S.; Bonifacio, C. S.; Zegkinoglou, I.; Sinev, I.; Choi, Y.-W.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Strasser, P.; et al. Highly Selective Plasma-Activated Copper Catalysts for Carbon Dioxide Reduction to Ethylene. *Nat. Commun.* **2016**, *7*, 12123.

(73) Wang, Z.; Yang, G.; Zhang, Z.; Jin, M.; Yin, Y. Selectivity on Etching: Creation of High-Energy Facets on Copper Nanocrystals for CO<sub>2</sub> Electrochemical Reduction. *ACS Nano* **2016**, *10*, 4559–4564.

(74) Liu, Y.; Chen, S.; Quan, X.; Yu, H. Efficient Electrochemical Reduction of Carbon Dioxide to Acetate on Nitrogen-Doped Nanodiamond. *J. Am. Chem. Soc.* **2015**, *137*, 11631–11636.

(75) Carmo, M.; Fritz, D. L.; Mergel, J.; Stolten, D. A Comprehensive Review on PEM Water Electrolysis. *Int. J. Hydrogen Energy* **2013**, *38*, 4901–4934.

(76) Singh, M. R.; Clark, E. L.; Bell, A. T. Thermodynamic and Achievable Efficiencies for Solar-Driven Electrochemical Reduction of Carbon Dioxide to Transportation Fuels. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, E6111–E6118.

(77) Vesborg, P. C. K.; Seger, B. Performance Limits of Photoelectrochemical  $CO_2$  Reduction Based on Known Electrocatalysts and the Case for Two-Electron Reduction Products. *Chem. Mater.* **2016**, 28, 8844–8850.

(78) Gupta, N.; Gattrell, M.; MacDougall, B. Calculation for the Cathode Surface Concentrations in the Electrochemical Reduction of  $CO_2$  in KHCO<sub>3</sub> Solutions. *J. Appl. Electrochem.* **2006**, *36*, 161–172.

(79) Birdja, Y. Y.; Koper, M. T. M. The Importance of Cannizzaro-Type Reactions during Electrocatalytic Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **201**7, *139*, 2030–2034.

(80) Bae, J. H.; Han, J.-H.; Chung, T. D. Electrochemistry at Nanoporous Interfaces: New Opportunity for Electrocatalysis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 448–463.

(81) Zhang, L.; Zhao, Z.-J.; Gong, J. Nanostructured Materials for Heterogeneous Electrocatalytic  $CO_2$  Reduction and Related Reaction Mechanisms. *Angew. Chem., Int. Ed.* **2017**, DOI: 10.1002/anie.201612214.

(82) Wang, H.; Turner, J. A. The Influence of Metal Ions on the Conductivity of Nafion 112 in Polymer Electrolyte Membrane Fuel Cell. J. Power Sources 2008, 183, 576–580.

(83) Electrical Conductivity of Aqueous Solutions. In CRC Handbook of Chemistry and Physics, 97th ed.; Haynes, W. M., Ed.; CRC Press/Taylor & Francis: Boca Raton, FL., 2016; pp 5–71.

(84) Kopljar, D.; Inan, A.; Vindayer, P.; Wagner, N.; Klemm, E. Electrochemical Reduction of  $CO_2$  to Formate at High Current Density Using Gas Diffusion Electrodes. J. Appl. Electrochem. **2014**, 44, 1107–1116.

(85) Wargo, E. A.; Hanna, A. C.; Çeçen, A.; Kalidindi, S. R.; Kumbur, E. C. Selection of Representative Volume Elements for Pore-Scale Analysis of Transport in Fuel Cell Materials. *J. Power Sources* **2012**, *197*, 168–179.

(86) Kulikovsky, A. A. The Regimes of Catalyst Layer Operation in a Fuel Cell. *Electrochim. Acta* **2010**, *55*, 6391–6401.

(87) Coridan, R. H.; Nielander, A. C.; Francis, S. A.; McDowell, M. T.; Dix, V.; Chatman, S. M.; Lewis, N. S. Methods for Comparing the Performance of Energy-Conversion Systems for Use in Solar Fuels and Solar Electricity Generation. *Energy Environ. Sci.* **2015**, *8*, 2886–2901.

(88) Hatsukade, T.; Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Jaramillo, T. F. Insights into the Electrocatalytic Reduction of  $CO_2$  on Metallic Silver Surfaces. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13814–13819.

(89) Ma, S.; Luo, R.; Moniri, S.; Lan, Y.; Kenis, P. J. A. Efficient Electrochemical Flow System with Improved Anode for the Conversion of  $CO_2$  to CO. J. Electrochem. Soc. **2014**, 161, F1124–F1131.

(90) Dufek, E.; Lister, T.; McIlwain, M. Bench-Scale Electrochemical System for Generation of CO and Syn-Gas. *J. Appl. Electrochem.* **2011**, *41*, 623–631.

(91) Fountaine, K. T.; Lewerenz, H. J.; Atwater, H. A. Efficiency Limits for Photoelectrochemical Water-Splitting. *Nat. Commun.* **2016**, 7, 13706.

(92) Yan, Y.; Gu, J.; Zeitler, E. l.; Bocarsly, A. B. Photoelectrocatalytic Reduction of Carbon Dioxide. In *Carbon Dioxide Utilisation*; Styring, P., Quadrelli, E. A., Armstrong, K., Eds.; Elsevier, 2015; pp 211–562.
(93) Joint Center for Artificial Photosynthesis. http://www.

solarfuelshub.org (Accessed May 24, 2017).

(94) Project a-leaf: "An Artificial Leaf: a photo-electro-catalytic cell from earth-abundant materials for sustainable solar production of  $CO_2$ -based chemicals and fuels". http://www.a-leaf.eu (Accessed May 24, 2017).