Carbon Dioxide Reduction

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Unraveling the Mechanism for the Sharp-Tip Enhanced Electrocatalytic Carbon Dioxide Reduction: The Kinetics Decide

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Abstract: *The electrocatalytic reduction reaction of carbon dioxide can be significantly enhanced by the use of a sharp-tip electrode. However, the experimentally observed rate enhancement is many orders of magnitudes smaller than what would be expected from an energetic point of view. The kinetics of this tip-enhanced reaction are shown to play a decisive role, and a novel reaction-diffusion kinetic model is proposed. The experimentally observed sharp-tip enhanced reaction and the maximal producing rate of carbon monoxide under different electrode potentials are well-reproduced. Moreover, the optimal performance shows a strong dependence on the interaction between CO_2 and the local electric field, on the adsorption rate of CO_2, but not on the reaction barrier. Two new strategies to further enhance the reaction rate have also been proposed. The findings highlight the importance of kinetics in modeling electrocatalytic reactions.*

Electrocatalytic reduction reaction of carbon dioxide (CO2RR) provides an attractive way to convert carbon dioxide (CO_2) to carbon monoxide (CO) from which more complex carbon-based fuels and feedstocks can be synthesized.[1–8] As CO_2 is a thermodynamically stable molecule,[1,2] tremendous efforts have been made in recent years to find suitable catalysts for electrocatalytic CO2RR as well documented in a recent review article.[3] However, low catalyst activity and low product selectivity remain to be the major problem.[3] One solution is to add alkali to stabilize adsorbed reagent species,[9–12] which can lead to a maximal producing rate of CO at an optimal electrode potential.[10–12] It was revealed that active reaction sites are often located at corners and ridges of the catalysts,[10,11,13] implying that local geometry of the catalyst surface may play an important role.

Very recently, Liu et al. proposed a fascinating, yet simple, strategy to significantly enrich the local concentration of CO_2 at the active site by placing catalytic tips on Au electrode.[14] It was experimentally observed that both electrocatalytic CO2RR rate and efficiency could increase when reducing the tip size from spherical particles (ca. 500 nm) to rods and then needles (≈ 50 nm). In comparison with the particles, the use of needles increased the reaction rate by almost 112 times, while the efficiency was enhanced up to 90%. It was believed that the sharp curvature of the tip could greatly enhance the local electric field to attract more alkali metal cations toward the catalytic tip, and consequently to increase the concentration of CO_2 around. Moreover, the enhanced local field was also believed to accelerate CO2RR by lowering the reaction barrier, which was found to be $72\,kJ\,mol^{-1}$, $44\,kJ\,mol^{-1}$ and $21\,kJ\,mol^{-1}$ for particles, rods and needles, respectively.[14] However, it can thus be obtained from Arrhenius equation that the reaction on needles should be accelerated about 7 orders of magnitude more than that on particles at room temperature, which is significantly faster than what was observed experimentally.[14] It is well known that a reaction is controlled both energetically and kinetically. Although the energetics alone appears to be adequate for many systems, it is certainly not good enough to describe the tip-enhanced reactions without considering the kinetics.

In this study, we present a novel reaction-diffusion kinetic model to resolve above mentioned mechanistic problem. Special attention is paid to the effect of field-induced reagent concentration on the tip surface. Our simulations successfully reproduce the key experimental findings for electrocatalytic $CO_2 \rightarrow CO$ reaction by Liu et al.[14] Several approaches to further improve the reaction performance are also suggested.

It is noted that in the experiments done by Liu et al.,[14] many tips were placed on the electrode surface to enhance the CO2RR reaction in the solution of K^+ (top-left inset in Figure 1). With the help of K^+, CO_2 was concentrated on the tips by tip-enhanced local electric field, and then reduced to CO with a Faradaic efficiency up to 90%. Such setup can be modeled by a periodic system with a cell containing one single tip (Figure 1), where CO_2 adsorbs on the electrode from the solution, diffuses on the surface, and is reduced at the tip. Since the tip induced electric field can lead to an extra mass transfer of CO_2 towards the tip other than concentration gradient,[14] the conventional reaction-diffusion equations[15] (RDEs) are not applicable for the sharp tip-enhanced CO2RR. Here, we derive the RDEs by including the field-induced extra mass transfer into the system's free-energy density functional[16] (Detailed derivation is given in the Supporting Information). For a position **r** on the surface, the RDEs read

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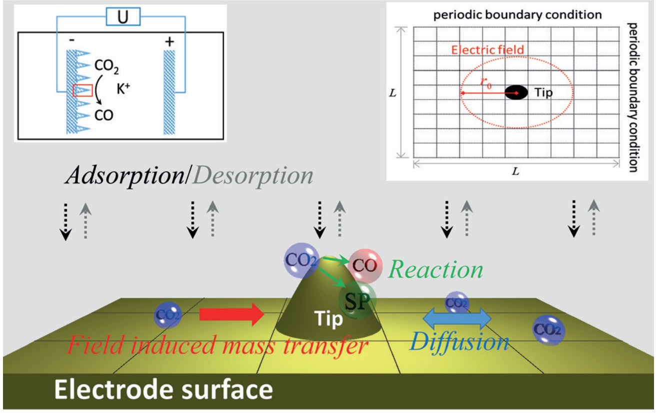

Figure 1. The kinetic model for CO2RR near a tip on electrode surface. SP denotes side products of CO2RR rather than CO. Insets show the experimental setup in Ref. [14] (top left) and the numerical simulation setup (top right).

$$\frac{\partial\theta(\mathbf{r})}{\partial t} = \varphi_0(1-\theta) - k_d\theta - k\theta - k_s\theta + D^2\theta - \frac{D}{k_B T}\cdot[\theta(1-\theta)V] \tag{1a}$$

$$\frac{\partial\theta_{CO}(\mathbf{r})}{\partial t} = k\theta - k_d^{CO}\theta_{CO} + D_{CO}{}^2\theta_{CO}, \tag{1b}$$

$$\frac{\partial\theta_{sp}(\mathbf{r})}{\partial t} = k_s\theta - k_d^{sp}\theta_{sp} + D_{sp}{}^2\theta_{sp} \tag{1c}$$

where k_B is the Boltzmann constant, T is the temperature. D and θ are the surface diffusion coefficient and the concentration normalized by its maximal value. The corresponding quantities with subscript "*co*" and "*sp*" are those for CO and possible side products (SP). φ_0, k_d, k, and k_s are rate constants of the effective adsorption, desorption, reaction from CO_2 to the main product CO, and the effective reaction to SP, respectively. The equilibrium CO_2 concentration for a surface without any reactions is $\theta_{eq} = \varphi_0/(\varphi_0 + k_d)$. When tips present, the tip-induced electric field U can accelerate the main and the side reactions as $k_{(s)}(U) = k_{(s),\eta=0}e^{-\lambda_{(s)}\eta_{(s)}(U)}$, where $\lambda_{(s)}$ and $\eta_{(s)}(U)$ are the apparent barrier-reducing coefficient and the overpotential of the main(side) reaction, respectively.

More importantly, the field also leads to extra mass transfer of CO_2[14] from the bulk to the electrode or from other parts of the electrode to the tip. Since the former is usually very limited,[17] we mainly consider the latter as the last term in Eq.(1a) with an effective potential $V(\mathbf{r}) = \alpha\theta U_{tip}\exp\{-\left|\mathbf{r}-\mathbf{r}_{tip}\right|^2/r_0^2$ where α is the interaction strength, r_0 is the characteristic length of the potential, $\mathbf{r}_{tip}$ is the location of the tip, and U_{tip} is the intensity of the electric field at the tip. The dependence of U_{tip} on the tip size R_{tip} can be fitted by the data in Ref. [14] as $U_{tip}(R_{tip}) = (u_0/u_p)(R_{tip}/R_p)^{-0.7}$ (Supporting Information, Figure S1), where u_0 is the electrode potential, u_p and R_p are the electrode potential and the size of the tip in a reference system as the one with spherical particles on Au electrode in Ref. [14]. Here and in other parts of the paper, quantities with subscript "*p*" denote the corresponding quantities in the same reference system. A detailed discussion about all the terms in the RDEs is presented in Supporting Information.

We apply the kinetic model to reproduce the reported sharp-tip enhanced CO2RR[14] by discretizing Eq. (1a-1c) on a $L \times L$ rectangle lattice with $N \times N$ grids and periodic boundary conditions (top-right inset in Figure 1; see the Supporting Information for details). It is found that sharp-tip enhanced CO2RR can be well reproduced with parameter values listed in Table I, where $k_B T$, the lattice size L and D are taken as basic units for parameter dimensionless. In Figure 2a, the dependence of the producing rate of CO averaged over the whole lattice,$v = (1/N^2)\sum_{i=1}^{N}\sum_{j=1}^{N} k_{ij}\theta_{ij}$, on the tip radius R_{tip} is presented, where $k_{ij}\theta_{ij}$ is the main reaction rate on the (*i,j*) grid. Compared with that on spherical particles ($R_{tip} = R_p$, indicated by the green arrow), the main reaction is accelerated about two orders of magnitude for needles ($R_{tip} = 0.1R_p$, the blue arrow). Meanwhile, the efficiency $e = v/(v + v_s)$ is also enhanced from a very low level to about 90 %, where $v_s = (1/N^2)\sum_{i=1}^{N}\sum_{j=1}^{N} k_{s,ij}\theta_{ij}$ is the averaged producing rate of SP.

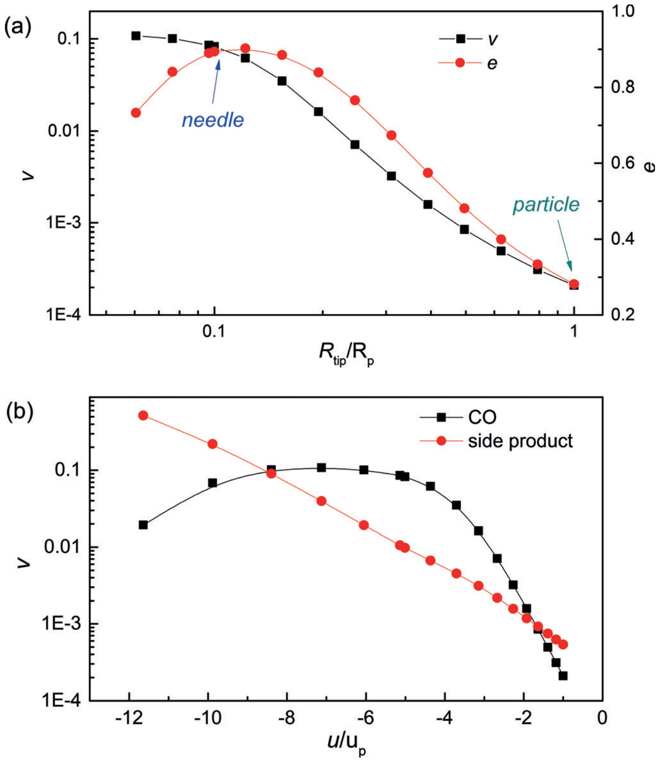

Figure 2. Reproducing the experimentally observed a) sharp-tip enhanced reaction and b) maximal producing rate of CO for varying electrode potentials. Parameters with subscript "*p*" denote their counterparts in the reference system with spherical particles on Au electrode surface as that in Ref. [14].

The reliability of the kinetic model is further validated by reproducing the experimentally observed maximal producing rate of CO under different electrode potentials.[10–12] In Figure 2b, the producing rates for both the main and side products as functions of the electrode potential u are plotted. Similar to those reported in literature,[10–12] v shows a typical volcano curve as the function of u. On the contrary, the side reaction is always accelerated by the increased u, in good agreement with the experiments as well.[12]

Table 1: Kinetic parameters for the experimentally observed sharp-tip enhanced CO2RR.[14]

Parameter	N	φ	θ_{eq}	r_0	α	λ	$\lambda_{(s)}$	$k_{\eta=0}$	$k_{s,\eta=0}$
Value	100	0.1	0.01	0.05	1	1.5	0.75	100	0.05

With the established kinetic model, key factors for the sharp-tip enhanced $CO_2 \rightarrow CO$ reaction can be identified. From the energetic point of view, one of the most important factors for CO2RR is the energy barrier of the main reaction. If there is a catalyst that can selectively further reduce the energy barrier of the main reaction, that is, the main reaction is of a larger rate constant k while other kinetic parameters are not affected, CO should be produced more quickly. In Figure 3, dependence of the CO producing rate v and efficiency e on the tip size R_{tip} is plotted for different k. On tips with large size, CO2RR can be accelerated remarkably when k increases (Figure 3a), and the efficiency is also noticeably enhanced (Figure 3b). However, for small tip size, v only increases slightly while e even drops. It already indicates that for the tip-enhanced reaction, the energy barrier alone is not the decisive factor that controls the overall reaction rate and efficiency.

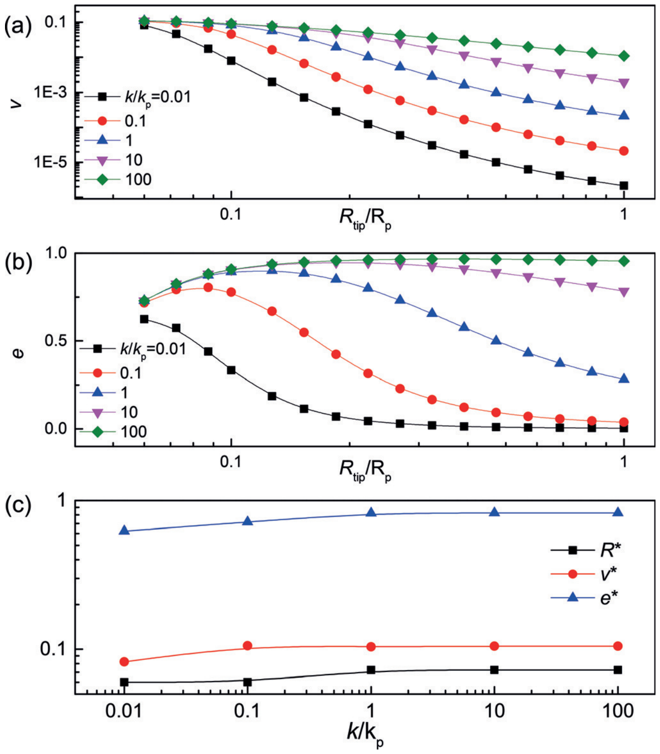

Figure 3. a) Reaction rate v of the main reaction $CO_2 \rightarrow CO$ and b) efficiency e as the function of the tip radius with different values of the rate constant k. c) Dependence of the optimal sharp-tip enhanced CO2RR performance on k, where R^*, v^*, and e^* are the tip size, CO producing rate, and efficiency when the optimal performance is achieved for a given k.

In order to find out the optimal sharp-tip enhancement of $CO_2 \rightarrow CO$ reaction for varying tip sizes, we define an order parameter as $F(R_{tip}) = ve$ based on the fact that there is usually a range of tip size in which the CO producing rate v is almost maximized while the efficiency e remains very high, e.g., those near $R_{tip} = 0.1R_p$ in Figure 2a and in Figure 3. The tip size R^* for the optimal performance can then be obtained by maximizing $F(R_{tip})$ as$F(R^*) = \max F(R_{tip})$, and the optimal performance can be described by the corresponding rate v^* and efficiency e^* forR^*. Quite interestingly, the optimal performance is robust to k especially for $k > k_p$ as shown in Figure 3c, implying that the main reaction has already been accelerated enough so that the optimal sharp-tip enhanced performance cannot be further enhanced by simply lowering the energy barrier of the main reaction. This observation is also consistent with the experimental observation that similar sharp-tip enhancement can be induced by electrodes of different materials.[14]

For catalysts without selectivity, that is, those lowering the barrier of both the main and the side reactions simultaneously (which is realized in our model by increasing the rate constants of both the main and side reaction with a fixed ratio k/k_s), the CO producing rate v can be enhanced obviously for large tips, e.g., $R_{tip} = R_p$, while it is depressed for small tips (Supporting Information, Figure S2a). For all tips, the efficiency e always decreases as k and $k_s$increase (Supporting Information, Figure S2b). Overall, the optimal sharp-tip enhancement is depressed by increasing the rate constants, and the optimal tip size moves towards larger values (Figure 4a). Moreover, if the catalyst only selectively catalyzes the side reaction, both of the rate and efficiency are

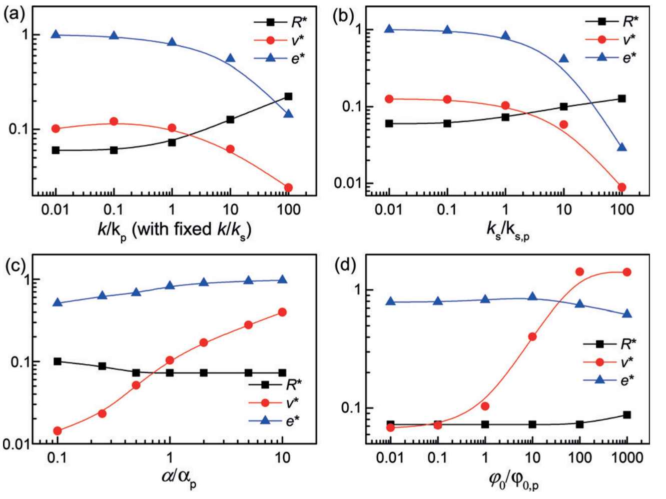

Figure 4. Optimal CO2RR performance depending on a) the rate constants of both the main and the side reactions which increase simultaneously with fixed ratio, b) the rate constant of the side reaction which is selectively accelerated by the electrode catalysis, c) the interaction strength between adsorbed CO_2 and the locally induced electric field, and d) the effective adsorption rate for CO_2 on the electrode surface. Quantities with superscript "*" are those for optimal CO2RR performance.

depressed when the rate constant k_s increases (Supporting Information, Figure S3), and consequently the optimal performance of the sharp-tip enhancement falls quickly with increasing k_s (Figure 4b).

The above findings indicate that energetic barriers of the reactions cannot be considered as the key factors for the sharp-tip enhancement of CO2RR. A possible explanation is that the main reaction on the tip is so fast that the kinetic process of mass transfer becomes the rate-determining step, a viewpoint also echoed by previous studies.[5,13] In the sharp-tip enhanced experiments, alkali cations have been added in to improve the overall reaction rate, and CO_2 attached to the cations can be driven to the position of more negative electric potential on the electrode surface, for example the tip.[14] Apparently, the interaction strength α between CO_2 and the electric field is a very important factor that should be considered for the sharp-tip enhanced CO2RR. It is found that both of the CO producing rate v and the efficiency e increase monotonically as α increases for tips of any size (Supporting Information, Figure S4). As a result, v^* of the optimal performance is greatly enhanced by increasing α, while e^* is also improved to be nearly 100% (Figure 4c). This observation demonstrates that the field-induced mass transfer on the surface is a key factor for the sharp-tip enhanced CO2RR: When the normal diffusion of CO_2 to the tip cannot match the fast reaction, the field-induced attraction can supply extra CO_2 to provide a better CO2RR performance.

As a part of the kinetic process, the adsorption of the reagent to the surface can also play an important role. A faster adsorption, on the one hand, increases directly the supply of CO_2 from the bulk to the tip, and on the other hand, provides more adsorbed CO_2 on other surface sites for diffusion or field-induced extra mass transfer. Simulations by our kinetic model reveal that the CO producing rate is always enhanced as the effective adsorption rate constant φ_0 increases, while the efficiency gives a maximum for an intermediate φ_0 (Supporting Information, Figure S5). The optimal performance shows that CO2RR can be greatly accelerated for large enough φ_0 at the expense of slightly lowering the efficiency (Figure 4d).

With all the simulation results, the underlying mechanism for the sharp-tip enhanced CO2RR can thus be revealed. It can be concluded that the sharp-tip enhanced reaction is a universal phenomenon for electrocatalytic chemical reactions. The sharp-tip enhancement can be effectively utilized when the lowering of the reaction barrier and the introduction of extra mass transfer of CO_2 both take place. This finding is in consistent with all the findings in the experiments.[14] However, it should be emphasized that the optimal performance of the sharp-tip enhanced CO2RR is mainly controlled by the kinetic rather than the energetic factors. It is due to a simple fact that without sufficient supply of CO_2, a further lowering of the reaction barrier has very small effects on the overall performance. Although the normal surface diffusion is often too slow to provide sufficient CO_2 for the fast reaction on the tip, the adsorption of CO_2 from the solution to the surface, along with the field-induced surface mass transfer from other sites to the tip, can overcome the difficulty to supply extra CO_2 for reactions and consequently lead to an enhancement of the overall reaction. Furthermore, similar to the main reaction, the side reaction can also be enhanced by the sharp-tip effect with the same reasons. The competition between the side reaction and the main reaction determines that the tip size for optimal CO2RR performance cannot be too small, as reflected by the robustness of R^* observed in Figure 3c and Figure 4.

In summary, we have established a novel reaction-diffusion kinetic model for sharp-tip enhanced CO2RR, and revealed that the kinetic of the tip-enhanced CO2RR reaction plays a decisive role. It has long been established that catalytic reaction is a complicated process controlled by both the thermodynamic and kinetic. However, in recent years, we have witnessed a trend that solely focuses on the role of the thermodynamics, particularly in theoretical modeling. The current study provides a convincing example to highlight the failure of this simplified approach. It is our hope that the kinetic modeling will become a routine practice in future mechanistic studies, which will certainly enhance our ability in designing new catalysts for practical applications.

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Conflict of interest

The authors declare no conflict of interest.

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