Electroreduction of CO$_2$ over Ag: A Multiscale Simulation

Ning Liu[1], Longfei Chen[1], Kai Deng[1], Tong Shi[1,2], Hao Feng[1], Ying Zhang[1], Dong Liu[1*], Qiang Li[1*]

1 School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

2 School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

*Corresponding author: liudong15@njust.edu.cn, liqiang@njust.edu.cn

ABSTRACT

Electrochemical CO$_2$ reduction reaction (CO$_2$RR) involves complicated processes spanning multiple scales, so understanding their effects on device performance is highly desired. Here, we present a multiscale strategy to predict the performance of an Ag-based H-type cell. The multiscale model consists of 1-D macro model, microkinetic model, and density functional theory (DFT) model. Free energy and barriers for CO$_2$RR and hydrogen evolution reaction (HER) over Ag(111) surface are first obtained from the DFT model. These energy values are then used to determine the reaction rates for CO$_2$RR and HER in the microkinetic model. These reaction rate values are finally imported into the macro model containing aqueous species. Using this multiscale model, we predicted the distribution of products and the partial current densities. We also described how factors such as CO$_2$ coverage, the adsorption energy of H$_2$O, and cathodic voltage affect electrochemical performance. Simulations under different CO$_2$ pressures are being implemented, which is of great significance for understanding the mechanism of high-pressure electrochemical reduction of CO$_2$. The investigation of electrochemical CO$_2$RR presented in this work is helpful for the rational design of a high-performance CO$_2$RR system.

Keywords: CO$_2$ reduction, electrochemical, multiscale simulation, density functional theory

NONMENCLATURE

Abbreviations	
CO$_2$RR	CO$_2$ reduction reaction
DFT	Density functional theory
kMC	Kinetic Monte Carlo

HER	Hydrogen evolution reaction
Symbols	
*	Adsorption species

1. INTRODUCTION

The electrochemical CO$_2$ reduction reaction offers a way to convert excessive greenhouse gases into fuels, which have been considered as an effective pathway to a sustainable carbon-neutral cycle[1]. To investigate the mechanism of CO$_2$RR, extensive effort have been made in the recent years. DFT provides a micro perspective to study the intrinsic properties of catalysts. For example, Zhang et al.[2] found that the H$_2$O could assist in the formation of CO over silver electrode surfaces using DFT calculations. However, the processes of CO$_2$RR involves not only the elementary reactions over the catalyst surface, but also the coverages of adsorbates, pH, the dimension of the device, and the transport of the species in the electrolyte. Singh et al.[3] constructed the transport model of electrochemical cell and studied the device components and operating conditions on its performance, but there was little consideration of micro mechanism. Multiscale simulation is a promising way to solve such a complex problem, which combines DFT calculations to macroscopic quantities. The current multiscale simulation of CO$_2$RR is mainly based on the combination of DFT calculation and kinetic Monte Carlo (kMC) method. Surface coverage and conversion frequency of catalyst are simulated by kMC method through the calculation of kinetic and thermodynamic properties. Although it does not involve the macro scale of the reactor, this method can be used to study the reaction path[4] and catalyst surface activity[5]. Singh et al.[6] developed a multiscale model using DFT and

transport model, but the effect of pressure on adsorption energy was not considered. Here we developed a multiscale model based on the theory proposed by Singh et al and induced the partial pressure. We identified the mechanism over Ag and predicted the current densities of products. We discussed how the kinetic parameters such as adsorption energy of CO_2 and H_2O affect the selectivity. The simulated performance is in good agreement with the experimental data.

2. METHOD

Fig. 1 shows an overview of our model in three scales and their connection. The Gibbs free energy of reactions and barriers for CO_2 reduction and hydrogen evolution are determined by fixed-potential DFT calculations[7-9] so that the rate constants and equilibrium constants of elementary steps are determined. The microkinetic model is built to calculate the reaction rate of CO_2RR and HER by the data from the last scale. Using production rates of H_2 and CO as boundary conditions, a macro model of the device describes the distribution of potential and the transport of species.
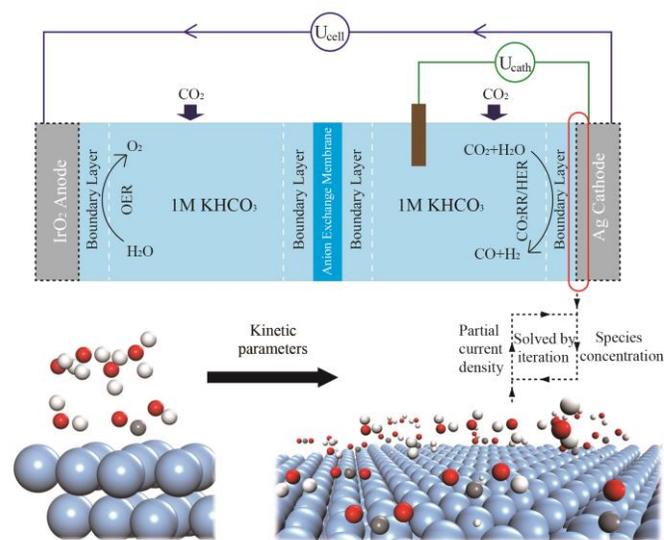

Fig. 1. Schematic illustration of multiscale model.

2.1 DFT model

All density functional theory (DFT) calculations were performed with Vienna ab initio simulation program (VASP)[10], using revised Perdew-Burke-Ernzerhof (RPBE) functional[11]. A 3×3 supercell with 4 layers was constructed, and the bottom two layers were fixed to simulate the bulk of the catalyst. Five explicit water molecules were added to describe the interaction between solvent molecules and adsorbates, respectively. A vacuum space of 30 Å was adopted for all

calculations in this work. The Debye length of 3 Å was used, which is corresponding to an electrolyte concentration of 1 M[12].

2.2 Microkinetic model

The electrochemical reduction of CO_2 involves three steps. In the first step, linear CO_2 molecular is activated by sharing electron density with catalyst surface[13], and forming bent $*CO_2^{\delta-}$. In the second step, the absorbed $*CO_2^{\delta-}$ combines with an H atom provided by explicit water and then forms absorbed COOH (**COOH) intermediate and hydroxyl ion. Finally, **COOH is dehydroxylated by another explicit water, producing *CO and hydroxyl ion. In the recent work of Tang et al[14], Volmer-Heyrovsky mechanism is proved to predominate over Ag (111). Consequently, we used Volmer-Heyrovsky mechanism to model HER over the catalyst.

2.3 Macro model

The continuum transport model of HiPD consists of four parts: cathode surface, anode surface, electrolyte, and anion exchange membrane. The thickness of AEM is taken as 50 μm. We assumed that there are no mass transfer resistances in the bulk electrolyte, and the diffusional resistance only exists in the boundary layers next to each solid-liquid interface. The anion exchange membrane has a fixed background charge concentration of +3.04 M, which is equivalent to 2.02 meq/g of ion exchange capacity and 75.2 g/m^2 of the density of Fumapem FAA-3-50.

3. RESULTS AND DISCUSSION

3.1 Model validation

In order to verify the reliability of the multiscale model, the following experiment was designed. We performed CO_2RR experiments in a customized H-type device. Both the cathodic and anodic chambers are filled with 1 M $KHCO_3$ and CO_2. The materials of anode and cathode are IrO_2 and Ag respectively, and the distance between electrode and membrane is 0.5 cm. An anion exchange membrane (Fumapem FAA-3-50) is located in the center of the two electrodes and has a thickness of 40~50 microns. The anodic and cathodic chambers are both kept in equilibrium with 1 atm CO_2. Ag/AgCl was used as the reference electrode to measure cathode potential. The current densities under different pressure were measured at potentials ranged from -0.4 to -1.1 V vs. reversible hydrogen electrode (RHE) with an interval of 0.1 V. Carbonaceous products and hydrogen were detected by gas-chromatography. Fig. 2 shows the

performance of the electrochemical cell in experiment. The selectivity of H_2 is higher than 20%, indicating that HER is typically competitive. Futhermore, Fig. 4 shows that the current density predicted by theoretical calculation is in good agreement with the experimental
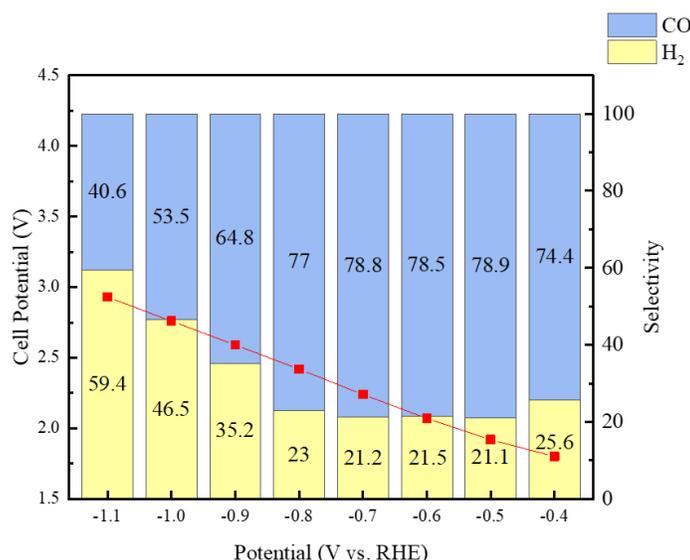

Fig. 2. Diagram of selectivity and cell potential at potentials varying from -0.4 to -1.1 V vs. RHE. (pH=7.93)

data.

3.2 Mechanism for CO₂RR over Ag(111)

The reduction of CO_2 starts from physisorbed linear $*CO_2$ reduced to chemisorbed $*CO_2^{\delta-}$, which has a bond angle of 128.6° and bond lengths of 1.27Å (the oxygen closer to the surface) and 1.26 Å. According to the Bader charge analysis, the charge of $*CO_2^{\delta-}$ relative to $*CO_2$ is approximately -0.8e, indicating that partial electron transfer reaction occurs. The process from $*CO_2$ to $*CO_2^{\delta-}$ is thermodynamically spontaneous and has an energy barrier lower than 0.2 eV at a high cathodic potential. Moreover, the energy barrier of reduction of $*CO_2^{\delta-}$ is reduced by 0.3 eV compared to the direct reduction of $*CO_2$ according to our calculation. Therefore, $*CO_2^{\delta-}$ rather than $*CO_2$ is the reactant that is reduced to obtain $**COOH$ over Ag(111) surface. The hydrogenation of $*CO_2^{\delta-}$ is the second step of CO₂RR, which contains the transfer of $(1-\delta)\cdot e^-$ and completes the first proton-coupled electron transfer reaction. This reaction has the highest energy barrier of ~0.76 eV at most electrode potential and increases slightly with the decrease of potential, hence it is the rate-determining step (RDS) for the formation of CO. The transfer coefficient (the calculated slope of free energy vs. cathodic potential) is -0.007. A small transfer coefficient leads to a high energy barrier despite the potential changes. Therefore, the

formation rate of $**COOH$ largely depends on the concentration of $*CO_2^{\delta-}$ (e.g. the coverage of $*CO_2^{\delta-}$) rather than potential according to the law of mass action. This makes the low coverage of $*CO_2$ resulted from limited CO_2 mass transport greatly affect the reaction rate of RDS, thus causing the CO current density to flatten at low potential.
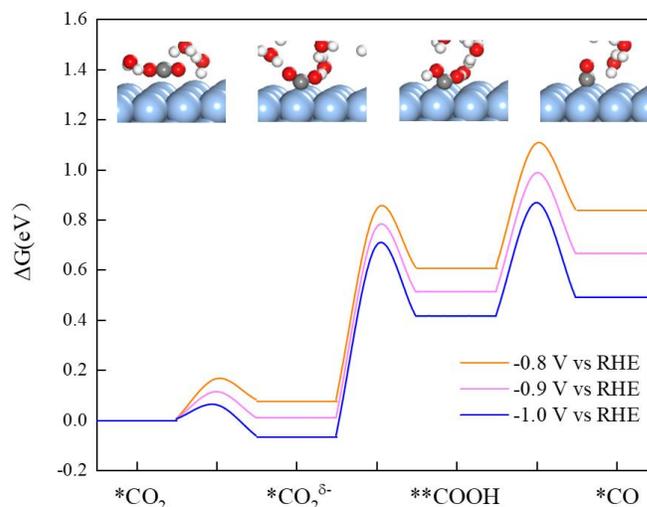

Fig. 3. Free energy diagram of CO₂RR to produce CO over Ag(111) at -0.8, -0.9, and -1.0 vs RHE. (pH=7.93)

3.3 Prediction of partial current density

The dependence of the partial current densities for gas products as a function of cathodic potentials is shown in Fig. 4. The H_2 current density is suppressed when the cathodic potential is higher than -0.8 V vs. RHE because the energy barrier for RDS of HER is at least 0.28 eV higher than that for the reduction of $CO_2^{\delta-}$. The simulation results show that the CO partial current density is higher than the experimental values and the H_2 partial current density is lower than the experimental values when the cathodic potential is relative low. That is because CO₂RR on the silver surface is very sensitive to the adsorption energy of gas molecules. The DFT model overestimates the adsorption energy of CO_2 at low cathodic potential, resulting in a higher CO_2 coverage. Furthermore, this phenomenon also indicates that the the selectivity of CO at low potential is limited not only by the poor transport condition for CO_2 at ambient pressure, but also by the increase of adsorption energy of H_2O with the increase of potential. According to DFT calculations, the transfer coefficient of CO_2 adsorption energy is 0.06 while the value of H_2O is 0.14. This means that the growth rate of H_2O adsorption energy is higher than that of CO_2, which aggravates the evolution of hydrogen at low potential and makes the predicted
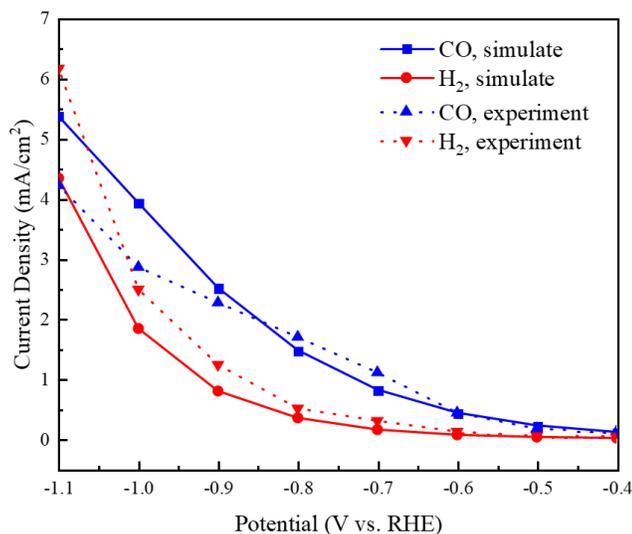
Fig. 4. Predicted and measured current densities at potentials varying from -0.4 to -1.1 V vs. RHE. (pH=7.93)

selectivity of CO decrease with potential to some extent as shown in Fig. 4.

4. CONCLUSION

We developed a multiscale model for electrochemical CO_2RR and simulated the surface chemistry of the cathode, the microkinetic process of surface reactions, and the transport of the species in a H-type electrochemical cell. We predicted the production of gases over Ag(111) with a small error and identified that $*CO_2^{\delta-}$ is the key intermediate at the processs of CO_2RR. The mass transport limitation and the increase of the adsorption energy of H_2O at the low cathodic potential both result in the decrease of CO selectivity. This model helps to predict the partial current density of the Ag-based electrochemical cell, and it also shows that increasing the pressure of CO_2 and modifying the catalyst to reduce the adsorption of H_2O is promising, providing the guidance for the rational design of CO_2RR system.

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