Supporting Information

Improving Interfacial Electron Transfer via Tuning Work Function of Electrodes for Electrocatalysis: From Theory to Experiment

Tao Liu,† Cong Xi,† Cunku Dong,*,†,‡ Chuanqi Cheng,† Jiayi Qin,† Shanwei Hu,§ Hui Liu† and Xi-Wen Du*,†,‡

†Institute of New Energy Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, P. R. China
‡Key laboratory of Advanced Ceramics and Machining Technology, Tianjin University, Tianjin 300072, P. R. China
§National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Index

1. Experimental Details
1.1. Electrode Preparation
1.2. Electrochemical Measurements and Product Analysis
2. Calculation of Barrier Height $U_m$
3. Relation between Work Function of Metals and Potential of Zero Charge
4. Figure S1-S6
5. Table S1
1. Experimental Methods

1.1. Electrode Preparation:

For the powder sample, the catalyst ink was prepared by mixing 4 mg powder, 0.2 mL isopropyl alcohol, 0.2 mL ultrapure water and 20 μL Nafion solution (5 %) under sonication for 30 minutes. 10 μL catalyst ink was dripped onto glassy carbon electrode with an area of 0.196 cm².

1.2. Electrochemical Measurements and Product Analysis:

The potential of zero-charge (PZC) of a material is obtained by plotting its differential capacitance curve. We use the same electrochemical system with CO₂ electroreduction to obtain the PZC of the electrode during the reaction. The test used a constant potential step method, using the resistive-potential curves were recorded from -2.0V — 2.0 V (vs. SHE) at 1000 Hz with an incremental potential of 50 mV. And then, we can convert the resistance (R) into a differential capacitor (C_d) by the formula (1). The potential in the curve corresponding to the minimum value of the differential capacitance is the potential of zero charge.

\[ C_d = \frac{1}{2\pi f R} \]  

(1)

Where \( C_d \) represents the differential capacitance; \( f \) represents the frequency of the alternating current in the test; and \( R \) represents the resistance obtained by the test.

The electrochemical CO₂ reduction reaction was carried out in a two-compartment cell by using electrochemical workstation (CHI601E), with graphite as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The two-compartment cell was separated by a Nafion-115 proton exchange membrane. The electrolyte used in the experiment was 0.1 M KHCO₃ saturated with CO₂ gas (pH= 6.8).

The applied potentials were measured against a saturated calomel electrode (SCE) and converted to reversible hydrogen electrode (RHE) reference scale using \( E(\text{RHE}) = E(\text{SCE}) + 0.0591 \times \text{pH} + 0.242 \) V. Prior to electrochemical reduction process, CO₂ gas was delivered into the electrolyte at a rate of 40 sccm controlled by a mass flow controller (MFC, MKS Instruments Inc.) for 40 minutes to make it saturated. Before product analysis, the pre-electrolysis was performed for 30 min in order to pre-reduce electrode and activate electrode.
During the test processes, CO\(_2\) gas was delivered into the electrolyte at a rate of 20 sccm. Constant-potential electrolysis, at the potential of -1.1 V to -0.5 V vs. RHE, were performed in CO\(_2\)-saturated 0.1 M KHCO\(_3\) at room temperature. The outlet gas was vented directly into the gas-sampling loop and the gaseous products of CO\(_2\) electrocatalytic reduction were analyzed by an online gas chromatography (GC) (Agilent 7890B). The Faradaic efficiency (FE) of the gaseous product was calculated by the following equation:

\[
FE(\%) = \frac{nZF}{Q} \times 100\% = \frac{m_0 \times (A/A_0) \times \nuZF}{M \times i} \times 100\%
\]

where \(n\) is the amount of substance, \(Z\) the number of transferred electron (for example, CO is 2), \(F\) the Faraday constant (96485 C·mol\(^{-1}\)), \(m_0\) the amount of standard gas, \(A\) the peak area of detection, \(A_0\) the peak area of standard gas, \(\nu\) is the gas flow rate (20 sccm), \(M\) the relative molecular mass, \(i\) the instantaneous current.

The liquid products were analyzed by \(^1\)H nuclear magnetic resonance spectroscopy (\(^1\)H NMR) (Bruker AVANCE III, 400MHz). Samples were prepared by mixing 500 μL electrolyte with 100 μL D\(_2\)O (99.9%) and 10 μL DMSO (0.5505 g·μL\(^{-1}\)). The Faradaic efficiency (FE) of the gaseous product \(j\) was calculated by the following equation:

\[
FE(\%) = \frac{nZF}{Q} \times 100\%
\]

where \(n\) is the product moles number, \(Z\) the number of transferred electron (for example, HCOOH is 2), \(F\) the Faraday constant, \(Q\) the total transfer charge.

The partial current density of CO (\(j_{CO}\)) is calculated by the following equation:

\[
j_{CO} = j_{total} \times FE_{CO}
\]

where \(j_{total}\) is total current density during the electrolysis. \(j_{CO}\) and \(FE_{CO}\) are the partial current density and Faradaic efficiency of CO.

The energy efficiency (EE) was calculated by the following formula:

\[
EE = \frac{E_{eq} \times FE}{E_{eq} + \eta} \times 100\%
\]

where the \(E_{eq}\) is the theoretical equilibrium potential. \(\eta\) is the overpotential and FE refers to the Faradaic efficiency of the certain product.
The Tafel slopes were calculated from the partial derivative of the overpotential with respect to the log of the current:

\[
Tafel \, slope = \left[ \frac{\partial \eta}{\partial \log j_{CO}} \right]
\]  

(6)

\[
\eta(V) = E(V) - 0.11(V)
\]  

(7)

where \( \eta \) is the overpotential of the CO\(_2\) reduced to CO, and \( j_{CO} \) is the partial current density of CO.

The Electrochemical surface area (ECSA) was calculated by the following equation:

\[
ECSA = R_f \cdot S
\]  

(8)

\( S \) is the geometric surface area of the electrode and the roughness factor \( R_f \) was estimated from the ratio of double-layer capacitance \( C_{dl} \) for the working electrode to the corresponding smooth metal electrode (the specific capacitance of the smooth metal is generally 20-60 \( \mu \)F \cdot cm\(^{-2}\), herein, using the midpoint specific capacitance of 40 \( \mu \)F \cdot cm\(^{-2}\)). The experiments were performed at \( \text{N}_2 \)-saturated 0.1 M KHCO\(_3\) by sweeping potential between -0.2 to -0.1 V vs. RHE. The capacitive currents were analyzed by taking half of the difference in current density at -0.15 V vs. RHE and plotted as a function of scan rate. The slope value of the fitted line is the \( C_{dl} \).

2. Calculation of Barrier Height \( U_m \)

In the double layer model, an electrode in solution is covered by a layer of water molecule, and solvated molecule (e.g. CO\(_2\)) is separated from the electrode by this water layer. The water layer causes a potential energy barrier whose height varies with the electrode potential and could be calculated by considering the energy change (\( \Delta E \)). The energy change \( \Delta E \) is equal to the energy barrier height for the electron at the Fermi level to tunnel through.

The value of \( \Delta E \) was determined by use of the following thermodynamic cycle:
\[ e^- (m) + H_2O(ads) \xrightarrow{\Delta E} H(ads) + OH^- \]
\[ \text{H}_2O(ads) + e^- \xrightarrow{\Delta H(ads, H)} H + OH^- \]
\[ H_2O + e^- \xrightarrow{\Delta H(diss, H-OH)} H + e^- + OH^- \]

Therefore

\[ \Delta E = \Delta H(ads, H) - \Delta H(affinity) + \Delta H(diss, H-OH) + \Phi - \Delta H(ads, H_2O) \]
\[ = -192.8 - 176.4 + 492.6 + \Phi - \Delta H(ads, H_2O) \text{kJ·mol}^{-1} \]
\[ = 123.4 + \Phi - \Delta H(ads, H_2O) \text{kJ·mol}^{-1} \]

where \( \Phi \) is the work function of metal electrode.

The term \( \Delta H(ads, H_2O) \) contains two contributions, one arises from image-dipole interaction and another from field-dipole interaction. The contribution from image-dipole interaction is -2.9 kJ·mol\(^{-1}\).\(^{S1}\) It is found that barrier height is not greatly impacted by the potential of electrode.\(^{S1}\) For instance, the barrier height increases by 1.35 kJ\(^{-1}\) with an increase of potential by 0.1 V.

Hence, \( \Delta E \) can be obtained at the potential of zero charge

\[ \Delta E = (123.4 + 2.9) \text{kJ·mol}^{-1} \]
\[ = 126.3 + \Phi \text{kJ·mol}^{-1} \]
\[ = 1.32 + \Phi' \text{eV} \]

where the unit of \( \Phi' \) is “eV.” As \( \Delta E \) is equal to energy barrier height \( U_m + \Phi^M \) with respect to the Fermi level, according to eqs.3 in the maintext. \( U_m \) is the maximum value at the parabolic energy barrier \( U(z) = U_m - f(z)^2/2 \). In other words, the barrier height \( U_m + \Phi^M \) is the energy change of an electron from the Fermi level of the metal electrode to the ground state of the water layer. Thus, the value of \( U_m \) is calculated to be 1.32 eV with respect the zero energy at infinity in a vacuum.

Reference

3. Relation between Work Function of Metals and Potential of Zero Charge

As shown in the Scheme S1, the electrode potential can be calculated in terms of the Galvani potential differences across the interphases as

\[
E = m_1 \Delta^s \Phi_{test} - m_2 \Delta^s \Phi_{ref} + m_2 \Delta^m \Phi
\]

Where \( \Delta \Phi \)'s are the Galvani potential differences across the various interfaces; superscripts \( m_1 \) and \( m_1' \), \( m_2 \) and \( s \) represent metals \( m_1, m_1', m_2 \) and the solution, respectively. \( m_1 \) and \( m_1' \) are the same metals. When the charge density on the test electrode is zero (i.e. at the potential of zero charge, PZC), the electrode potential becomes

\[
E_{q=0}^{m_1} = m_1 \Delta^s \Phi_{q=0} - m_2 \Delta^s \Phi_{ref} + m_2 \Delta^m \Phi
\]

As these two metals in contact are in electronic equililbrium, the electrochemical potentials of two metals are equal

\[
\bar{\mu}_e^{m_1'} = \bar{\mu}_e^{m_2}
\]

Since \( m_1 \) and \( m_1' \) are the same metals, we get

\[
\Phi^{m_2} - \Phi^{m_1'} = (\mu_e^{m_2} - \mu_e^{m_1})/F
\]

where \( \bar{\mu}_e^{s} \) and \( \mu_e^{s} \) are the electrochemical and the chemical potentials of the electron, respectively.

Since the Volta potential difference at the metal- solution interface is zero at PZC \( (q=0) \), we get

\[
m_1 \Delta^s \Phi_{q=0} = m_1 \Delta^s g_{q=0}
\]

where \( m_1 \Delta^s g \) is the surface potential difference across the metal-solution interface at PZC. When the two phases are brought in contact with each other, the changes in the orientation of the solvent dipoles and the electron overlap at the metal surface should be considered, Thus

\[
m_1 \Delta^s g = \chi^{m_1} - \chi^s + \delta \chi
\]

where \( \chi^{m_1} \) and \( \chi^s \) are the surface potentials of the free \( m_1 \) and \( s \) phases, i.e., in contact with vacuum.

By inserting eqs. 3-5 into eqs. 2

\[
E_{q=0}^{m_1} = \chi^{m_1} - \chi^s + \delta \chi + \left( \mu_e^{m_2} - \mu_e^{m_1} \right)/F - m_2 \Delta^s \Phi_{ref}
\]
It may be noted at PZC that

\[- \mu_e^m + F \chi^m = \phi^m\]  \hspace{1cm} (7)

where \( \phi^m \) is the work function of \( m \). Therefore, from eqs. 6 and 7 we have by dropping superscript \( m \) and putting \( m_2 = \text{ref} \),

\[E_q = 0 = (\Phi/F) - \chi^s + \delta \chi - \text{ref} \Delta \phi + \left( \mu^{\text{ref}}_e / F \right)\]  \hspace{1cm} (8)

**Scheme S1.** Schematic illustration of electrode potential measurement
**Figure S1.** Schematic illustration of the microscopic structure of an EDL in the absence the electrified metal-solution interface (a) and the metal-water interface optimized by DFT simulation without applying an external electric field (b). In the absence of an external electric field, water dipoles are randomly distributed above Ag electrode.
Figure S2. Angle-resolved high-resolution O 1s XPS spectra of NaBH$_4$-Ag at the incidence angle of (a) 30° and (b) 90° after CO$_2$ reduction electrolysis. The peak at 532-532.5 eV is assigned to the molecular oxygen species (O$_M$), whereas the peak at 533-533.4 eV arises from the oxygen in hydroxyl of physically adsorbed H$_2$O (O$_{OH}$).
**Figure S3.** Angle-resolved high-resolution O 1s XPS spectra of ER-Ag after initial CO$_2$ reduction electrolysis at the incidence angle of (a) 30° and (b) 90°, after electrolysis at -1.1 V vs. RHE in CO$_2$-saturated 0.1 M KHCO$_3$ for 40 minutes. The peak at 532-532.5 eV is assigned to the molecular oxygen species (O$_M$), whereas the peak at 533-533.4 eV arises from the oxygen in hydroxyl of physically adsorbed H$_2$O (O$_{OH}$).
Figure S4. High-resolution O 1s XPS spectra of ER-Ag before initial CO$_2$ reduction electrolysis (Ag$_2$O powder). The peak at 529.5 eV is attributed to the lattice oxygen (O$_L$) of Ag-O, and the peak at 530.8 eV is assigned to the atomic oxygen incorporated into the bulk (O$_A$).
Figure S5. The UPS of Au standard sample. The pure Au foil used as the standard sample was cleaned by ion sputtering, and the following spectral was obtained by UPS test. Meanwhile, the Fermi edge of the instrument was also calibrated with the Fermi edge of the Au foil ($E_{\text{F}} = -9.54 \text{ eV}$).
Figure S6. (a) Calculated $C_{dl}$ of each working electrode. Cyclic voltammetry (CV) curves of (b) NaBH$_4$-Ag, (c) ER-Ag, (d) Ag MPs at different scan rates (from 5 mV·s$^{-1}$ to 30 mV·s$^{-1}$). The experiments were performed at 0.1 M KHCO$_3$ by sweeping potential between -0.2 to -0.1 V vs. RHE.
Table S1. Electrochemical Parameters for Calculating ECSA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{dl}$ (mF·cm$^{-2}$)</th>
<th>$R_f$</th>
<th>$S$ (cm$^2$)</th>
<th>ECSA (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBH$_4$-Ag</td>
<td>0.78</td>
<td>19.50</td>
<td>0.196</td>
<td>3.822</td>
</tr>
<tr>
<td>ER-Ag</td>
<td>0.92</td>
<td>23.00</td>
<td>0.196</td>
<td>4.508</td>
</tr>
<tr>
<td>Ag MPs</td>
<td>2.25</td>
<td>56.25</td>
<td>0.196</td>
<td>11.025</td>
</tr>
</tbody>
</table>