# Supporting Information Disappearance of Electric Double Layer Effects on Electrochemical Reactions: the Case of a Chemisorbed Small Species on a Metal Surface at the Electrode/Electrolyte-Solution Interface

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#### S1 Theoretical Method

### S1.1 Three-Dimensional Reference Interaction Site Model Self-Consistent Field (3D-RISM-SCF) Theory

As 3D-RISM-SCF has been described in detail in the literature,<sup>1</sup> only a brief summary of the framework is provided here. The equations are given in atomic units, unless otherwise stated. From the variational principle of free energy, the Kohn–Sham equation is obtained  $as^2$ 

$$\left[-\frac{1}{2}\nabla^2 + V_{\rm ps} + V_{\rm h} + V_{\rm xc} + V_{\rm sol}\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}),\tag{s-1}$$

where  $\psi_i$  is the Kohn–Sham orbital,  $V_{ps}$  is the nuclear attraction potential,  $V_h$  is the Hartree potential,  $V_{xc}$  is the exchange-correlation potential, and  $V_{sol}$  is the electrostatic potential generated by the solvent. The electron density  $\rho^U$  is given by

$$\rho^{\mathrm{U}}(\mathbf{r}) = \sum_{i} f_{i} |\psi_{i}(\mathbf{r})|^{2}, \qquad (s-2)$$

where  $f_i$  is the occupation number of the *i*th orbital given by the Fermi–Dirac function,<sup>3</sup>

$$f(\epsilon) = \frac{2}{1 + \exp\left(\frac{\epsilon_i - \mu_e}{k_B T}\right)},\tag{s-3}$$

where  $\epsilon_i$  is the energy and  $\mu_e$  is the chemical potential of an electron, *i.e.*, Fermi level. In this equation, a closed-shell electronic structure is assumed. The electric potential of electrochemical systems is determined using  $\mu_e$  in this study.

The 3D-RISM equation is given by  $^{2,4}$ 

$$h_{\gamma}(\mathbf{r}) = c_{\alpha}(\mathbf{r}) * \left\{ \omega_{\alpha\gamma}^{\mathrm{VV}}(r) + \rho_{\alpha}^{\mathrm{V}} h_{\alpha\gamma}^{\mathrm{VV}}(r) \right\}, \qquad (s-4)$$

where "\*'' denotes a convolution integral,  $\rho_{\alpha}^{V}$  is the average number density of the  $\alpha$ th solvent

site,  $\alpha$  and  $\gamma$  denote the atomic sites of solvent,  $\omega_{\alpha\gamma}^{VV}(k)$  is the intramolecular correlation function between the  $\alpha$ th and  $\gamma$ th solvent sites, and  $h_{\gamma}(\mathbf{r})$  and  $c_{\alpha}(\mathbf{r})$  are the total and direct correlation functionals, respectively. The superscript VV symbolizes the solvent–solvent pair correlation function. The density distribution function of the solvent site  $\gamma$  is given by  $g_{\gamma}(\mathbf{r}) = h_{\gamma}(\mathbf{r}) + 1$ . Because Eq. (s-4) has two unknown functions,  $\mathbf{h}$  and  $\mathbf{c}$ , the Kovalenko– Hirata closure,<sup>2</sup>

$$h_{\gamma}(\mathbf{r}) + 1 = \begin{cases} \exp\{\chi_{\gamma}(\mathbf{r})\} & (\chi_{\gamma} \le 0), \\ 1 + \chi_{\gamma}(\mathbf{r}) & (\chi_{\gamma} > 0), \end{cases}$$
(s-5)

$$\chi_{\gamma}(\mathbf{r}) = -\beta u_{\gamma}(\mathbf{r}) + h_{\gamma}(\mathbf{r}) - c_{\gamma}(\mathbf{r}), \qquad (s-6)$$

was used in this study. In Eq. (s-6),  $\beta$  is equal to  $1/k_BT$  and  $u_{\gamma}$  is the site-site interaction potential given as the sum of the electrostatic and Lennard-Jones (LJ) potentials,

$$u_{\gamma}(\mathbf{r}) = q_{\gamma}^{\mathrm{V}} \left\{ V_{\mathrm{nuc}}(\mathbf{r}) - V_{\mathrm{h}}(\mathbf{r}) \right\} + \sum_{j} 4\varepsilon_{j\gamma} \left\{ \left( \frac{\sigma_{j\gamma}}{|\mathbf{r} - \mathbf{R}_{j}|} \right)^{12} - \left( \frac{\sigma_{j\gamma}}{|\mathbf{r} - \mathbf{R}_{j}|} \right)^{6} \right\}, \qquad (s-7)$$

where  $\sigma_{j\gamma}$  and  $\varepsilon_{j\gamma}$  are parameters of the LJ potential defined by the *j*th and  $\gamma$ th atomic cites,  $q_{\gamma}^{\rm V}$  is the charge on the  $\gamma$ th solvent site,  $\mathbf{R}_j$  is the *j*th solute atomic site, and  $V_{\rm nuc}$  is the electrostatic potential generated by the nuclear charges on the solute.  $V_{\rm h}(\mathbf{r})$ , which is originally used as the interaction potential in Eq. (s-1) by negatively charged electrons, has a negative sign.

The free energy of the electrochemical system is defined using the grand potential  $\Omega$  given as

$$\Omega = E_{\rm es} + \Delta \mu - \mu_{\rm e} N_{\rm e}, \qquad (s-8)$$

where  $E_{\rm es}$  is the internal energy of the electrode system calculated using the density functional theory (DFT) method,  $\Delta \mu$  is the solvation free energy, and  $N_{\rm e}$  is the total number of electrons.  $\Delta \mu$  is given by<sup>2</sup>

$$\Delta \mu = \sum_{\gamma} \frac{\rho_{\gamma}^{\mathrm{V}}}{\beta} \int \frac{1}{2} \left\{ h_{\gamma}(\mathbf{r}) \right\}^{2} \Theta \left( -h_{\gamma}(\mathbf{r}) \right) - c_{\gamma}(\mathbf{r}) - \frac{1}{2} h_{\gamma}(\mathbf{r}) c_{\gamma}(\mathbf{r}) d\mathbf{r}, \qquad (s-9)$$

where  $\Theta(x)$  is the Heaviside step function. The electrostatic potential generated by the solvent is given by

$$\nabla^2 V_{\rm sol}(\mathbf{r}) = -4\pi \left\{ \sum_{\gamma} \rho_{\gamma}^{\rm V}(-q_{\gamma}^{\rm V})g_{\gamma}(\mathbf{r}) \right\},\tag{s-10}$$

and applied in Eq. (s-1). In Eq. (s-10),  $q_{\gamma}^{\rm V}$  is assigned a negative sign to account for interactions with electrons.

The finite charge correction is not needed to solve Eq. (s-1) because the entire system consisting of a solute (*i.e.*, the electrode and reactant) and solvent is charge neutral. However,  $V_{\text{nuc}}(\mathbf{r}) - V_{\text{h}}(\mathbf{r})$  in Eq. (s-7) represents the electrostatic potential generated by the charged solute. Thus, the formula described in the next section is adopted for the 3D-RISM calculations included in the 3D-RISM-SCF method.

#### S1.2 Theoretical Formula for Charged Materials

We have presented a theoretical formula to determine the solvation structure around a charged material comprising an electrode in our previous study.<sup>5</sup> This formula is based on that proposed by Vyalov et. al.,<sup>6</sup> which includes the contribution of an infinitely thin charged layer to the solvation structure using an analytical framework, thereupon the 3D-RISM calculation (i.e., without DFT calculation) of a charged slab can be performed. An infinitely thin charged layer is not sufficiently suitable for 3D-RISM-SCF because the electrons are spatially distributed. Therefore, we consider a charged slab with a finite thickness, where the slab surface is parallel to the x-y plane. Its electrostatic potential interaction with

solvent is then given by

$$u_{\gamma}^{l}(z) = q_{\gamma}^{\mathrm{V}} v^{\sigma_{\mathrm{L}}}(z). \tag{s-11}$$

 $v^{\sigma_{\rm L}}(z)$  is the electrostatic potential generated by the charged slab with a surface charge density  $\sigma_{\rm L}$ ,<sup>7</sup>

$$v^{\sigma_{\rm L}}(z) = -2\pi \times \begin{cases} \frac{\sigma_{\rm L}}{L}(z-z_0)^2 + \frac{\sigma_{\rm L}}{4}L + C & (|z-z_0| \le \frac{L}{2}) \\ \sigma|z-z_0| + C & (|z-z_0| > \frac{L}{2}), \end{cases}$$
(s-12)

where L and  $z_0$  are the thickness and center position of the charged slab, respectively. The results obtained are independent of the arbitrary parameter C because of the charge neutrality of the bulk homogeneous solvent. Therefore, C is omitted in this section.

The direct correlation function is partitioned as

$$c_{\gamma}(\mathbf{r}) = c_{\gamma}^{l}(\mathbf{r}) + c_{\gamma}^{s}(\mathbf{r}), \qquad (s-13)$$

where  $c_{\gamma}^{l}(\mathbf{r})$  is the long-range electrostatic interaction given by

$$c_{\gamma}^{l}(\mathbf{r}) = -\beta u_{\gamma}^{l}(z), \qquad (s-14)$$

and  $c_{\gamma}^{s}(\mathbf{r})$  is the short-range interaction. The 3D-RISM equation can then be rewritten as

$$h_{\gamma}(\mathbf{r}) = \left\{ c_{\alpha}^{l}(\mathbf{r}) + c_{\alpha}^{s}(\mathbf{r}) \right\} * \left\{ \omega_{\alpha\gamma}^{\mathrm{VV}}(r) + \rho_{\alpha}^{\mathrm{V}} h_{\alpha\gamma}^{\mathrm{VV}}(r) \right\}.$$
 (s-15)

Thus, the Kovalenko–Hirata closure becomes

$$h_{\gamma}(\mathbf{r}) + 1 = \begin{cases} \exp\{\chi_{\gamma}(\mathbf{r})\} & (\chi_{\gamma} \le 0), \\ 1 + \chi_{\gamma}(\mathbf{r}) & (\chi_{\gamma} > 0), \end{cases}$$
(s-16)

$$\chi_{\gamma}(\mathbf{r}) = -\beta u_{\gamma}^{s}(\mathbf{r}) + h_{\gamma}(\mathbf{r}) - c_{\gamma}^{s}(\mathbf{r}).$$
 (s-17)

 $u_{\gamma}^{s}$  is the sum of the Lennard–Jones and short-range electrostatic interactions,

$$u_{\gamma}^{s}(\mathbf{r}) = q_{\gamma}^{V} \left\{ V_{\text{nuc}}(\mathbf{r}) - V_{\text{h}}'(\mathbf{r}) \right\} + \sum_{j} 4\varepsilon_{j\gamma} \left\{ \left( \frac{\sigma_{j\gamma}}{|\mathbf{r} - \mathbf{R}_{j}|} \right)^{12} - \left( \frac{\sigma_{j\gamma}}{|\mathbf{r} - \mathbf{R}_{j}|} \right)^{6} \right\}, \quad (s-18)$$

where  $V'_{\rm h}$  is calculated from the difference between the electron density and slab charge per unit thickness  $\sigma_{\rm L}/L$ ,

$$\nabla^2 V_{\rm h}'(\mathbf{r}) = \begin{cases} -4\pi \left\{ \rho^{\rm U}(\mathbf{r}) - \left(\frac{-\sigma_{\rm L}}{L}\right) \right\} & (|z - z_0| \le \frac{L}{2}), \\ -4\pi \rho^{\rm U}(\mathbf{r}) & (|z - z_0| > \frac{L}{2}). \end{cases}$$
(s-19)

 $\sigma_{\rm L}$  has a negative sign because electrons have a negative charge. Note that the sum of the potentials,  $u_{\gamma}^{l}(\mathbf{r}) + u_{\gamma}^{s}(\mathbf{r})$ , reproduces the total potential  $u_{\gamma}$  in Eq (s-7).

The long-range part of the total correlation function is expressed as<sup>6</sup>

$$\begin{aligned} h_{\gamma}^{l}(\mathbf{r}) &= c_{\alpha}^{l}(\mathbf{r}) * \left\{ \omega_{\alpha\gamma}^{\mathrm{VV}}(r) + \rho_{\alpha}^{\mathrm{V}} h_{\alpha\gamma}^{\mathrm{VV}}(r) \right\} \\ &= -\beta \sum_{\alpha} \rho_{\alpha}^{\mathrm{V}} q_{\alpha}^{\mathrm{V}} \int_{\mathbf{R}} h_{\gamma\alpha}^{\mathrm{VV}}(|\mathbf{r} - \mathbf{r}'|) \left\{ v^{\sigma}(z') - v^{\sigma}(z) \right\} d\mathbf{r}' \\ &-\beta \sum_{\alpha(\alpha \neq \gamma)} \int_{\mathbf{R}} \frac{\delta(|\mathbf{r} - \mathbf{r}'| - l_{\alpha\gamma})}{4\pi l_{\alpha\gamma}^{2}} v^{\sigma}(z') d\mathbf{r}' - v^{\sigma}(z), \end{aligned}$$
(s-20)

where  $l_{\alpha\gamma}$  is the intramolecular distance between  $\alpha$  and  $\gamma$  sites, **R** indicates that integration is performed over the total space, and the electroneutrality condition of the bulk solvent,

$$\sum_{\alpha} q_{\alpha}^{\mathrm{V}} \int_{\mathbf{R}} \omega_{\alpha\gamma}^{\mathrm{VV}}(r) + \rho_{\alpha}^{\mathrm{V}} h_{\alpha\gamma}^{\mathrm{VV}}(r) d\mathbf{r} = 0, \qquad (s-21)$$

is applied. Because of the translational symmetry along the x and y directions of the flat charged slab,  $h_{\gamma}^{l}(\mathbf{r})$  in Eq. (s-20) depends only on the z coordinate (i.e., independent of the x and y coordinates). The third line of Eq. (s-20) can be calculated using the following equations:

$$\int_{\mathbf{R}} \frac{\delta(|\mathbf{r} - \mathbf{r}'| - l_{\alpha\gamma})}{4\pi l_{\alpha\gamma}^2} |z' - z_0| d\mathbf{r}'$$

$$= \begin{cases} |z - z_0| & \text{for } |z - z_0| > l_{\alpha\gamma}, \\ \frac{1}{2l_{\alpha\gamma}} \left\{ (z - z_0)^2 + l_{\alpha\gamma}^2 \right\} & \text{for } |z - z_0| \le l_{\alpha\gamma}, \end{cases}$$
(s-22)

and

$$\int_{\mathbf{R}(|z'-z_0| \le L/2)} \frac{\delta(|\mathbf{r} - \mathbf{r}'| - l_{\alpha\gamma})}{4\pi l_{\alpha\gamma}^2} \left\{ (z' - z_0)^2 - |z' - z_0| \right\} d\mathbf{r}'$$
  
=  $\frac{1}{2l_{\alpha\gamma}} \int_{|z'-z_0| \le L/2} \Theta(l_{\alpha\gamma} - |z - z'|) \cdot \left\{ (z' - z_0)^2 - |z' - z_0| \right\} dz'.$  (s-23)

 $\mathbf{R}(|z'-z_0| \leq L/2)$  in the first line of Eq. (s-23) indicates that integration is performed over the space  $|z'-z_0| \leq L/2$ , and cylindrical coordinates  $(\rho' = \sqrt{x'^2 + y'^2})$  are introduced.  $\Theta(l_{\alpha\gamma} - |z-z'|)$  is the Heaviside step function given by

$$\Theta(l_{\alpha\gamma} - |z - z'|) = \begin{cases} 0 & \text{for } l_{\alpha\gamma} - |z - z'| < 0, \\ 1 & \text{for } l_{\alpha\gamma} - |z - z'| \ge 0. \end{cases}$$
(s-24)

The one-dimensional integral along the z'-direction on the right-hand side of Eq. (s-23) can be solved numerically using fine grid points because the computational cost is low. Therefore, the computational cost to solve Eq. (s-20) is mainly determined by the second line. Fortunately, the second line can be rewritten as

$$-\beta \sum_{\alpha} \rho_{\alpha}^{\mathrm{V}} q_{\alpha}^{\mathrm{V}} \int_{\mathbf{R}} d\mathbf{r}' h_{\gamma\alpha}^{\mathrm{VV}}(|\mathbf{r} - \mathbf{r}'|) \left\{ v^{\sigma}(z') - v^{\sigma}(z) \right\}$$
$$= -\beta \sum_{\alpha} \rho_{\alpha}^{\mathrm{V}} q_{\alpha}^{\mathrm{V}} \int_{z'} \left\{ \int_{x',y'} h_{\gamma\alpha}^{\mathrm{VV}}(|\mathbf{r} - \mathbf{r}'|) dx' dy' \right\} \left\{ v^{\sigma}(z') - v^{\sigma}(z) \right\} dz'.$$
(s-25)

The integration over x' and y' in Eq. (s-25) is needed to be calculated only once before the iterative DFT and 3D-RISM calculations because of its dependence only on  $h_{\gamma\alpha}^{\rm VV}$ , that is, the total correlation function of the homogeneous bulk solvent. Therefore, only the integration over z' is needed to be performed during the 3D-RISM-SCF procedure, and the computational cost is almost negligible.

In the present approach, the DFT and 3D-RISM calculations can be directly connected in the sense that a unified grid-point basis set is used. The computational cost for the calculation of this study increases significantly because a large box is required to calculate the electric double layer. Thus, the SALMON program is highly suitable for this study owing to its applicability to large materials.

Dipole correction<sup>8</sup> is not used in this study because it causes only a small variation when the vacuum region is very large, as is the case in this study. Using the present approach, dipole correction can be applied by adding two charged slabs, whose electrostatic potential is defined by Eq. (s-12), to describe the potential shifts due to dipolar polarization.

In this study, the thickness L of the charge slab was set to 0.336 Å, and the charged slab was placed in the position of the surface Pt atom layer. In calculating  $h_{\gamma}^{l}(z)$  using Eq. (s-20), the contribution of the long-distance area depends on numerical errors due to the convergence threshold and fast Fourier transform procedure. Thus,  $h_{\gamma\alpha}^{\rm VV}$  values less than 1 × 10<sup>-10</sup> were rounded off during integration.

Our theoretical formula was derived simply by rewriting the original 3D-RISM equation, that is, no additional approximation was incorporated in our method as compared to the original 3D-RISM method. Therefore, numerous benchmarking results using the original 3D-RISM method is transferable for checking the validity of our method.

In our method, the electrode potential is given as the difference between the Fermi level and the computed SHE potential. To achieve the convergence of the chemical potential of electrons, we used the procedure proposed in a previous study.<sup>9</sup> Once the chemical potential is specified, we performed the constant- $N_{\rm e}$  calculations by varying  $N_{\rm e}$  many times until the specified chemical potential was obtained. The converged Fermi level was obtained by repeatedly performing the linear extrapolation where the system charge was treated as a function of the Fermi level. Through repeated calculations, we confirmed that the calculated Fermi level is a monotonic function of the system charge. More sophisticated algorithms have been proposed;<sup>10</sup> however, further improvement to the algorithm is beyond the scope of this study.

#### S1.3 Formula for Energy Calculation

The Kohn–Sham equation is solved in the same manner as that for conventional neutral systems because the entire system consisting of a solute (*i.e.*, the electrode and reactant) and solvent is charge neutral. However, there are additional considerations when calculating  $E_{\rm ele}$  because the charge neutrality of the total system consisting of a solute and solvent is not useful to calculate  $E_{\rm ele}$  given by

$$E_{\text{ele}} = \sum_{i} \left\langle \psi_{i} \left| \frac{1}{2} \nabla^{2} + V_{\text{nuc}} + \frac{1}{2} V_{\text{h}} + V_{\text{xc}} \right| \psi_{i} \right\rangle + \sum_{\text{nuc}} V_{\text{nuc}}(\mathbf{r}_{\text{nuc}}) Z_{\text{nuc}}(\mathbf{r}_{\text{nuc}}).$$
(s-26)

The second term is the nuclear-nuclear electrostatic interaction energy. In this study, the total electrostatic interaction energy  $E_{es}$  is rewritten as

$$E_{\rm es} = \sum_{i} \left\langle \psi_{i} \left| V_{\rm nuc} + \frac{1}{2} V_{\rm h} \right| \psi_{i} \right\rangle + \sum_{\rm nuc} V_{\rm nuc}(\mathbf{r}_{\rm nuc}) Z_{\rm nuc}(\mathbf{r}_{\rm nuc})$$
$$= \int \frac{1}{2} \left\{ V_{\rm nuc}(\mathbf{r}) + V_{\rm h}(\mathbf{r}) \right\} \cdot \left\{ \rho(\mathbf{r}) + \sum_{\rm nuc} \delta(\mathbf{r} - \mathbf{r}_{\rm nuc}) Z_{\rm nuc}(\mathbf{r}) \right\} d\mathbf{r} - \frac{1}{2} \sum_{\rm nuc} Z_{\rm nuc}^{2} \frac{\alpha}{\sqrt{\pi}},$$
(s-27)

where the Ewald method is applied using the parameter  $\alpha$ .<sup>11</sup> We further introduce a uniform background charge correction<sup>7</sup>

$$\frac{1}{2}\left\{V_{\text{nuc}}(\mathbf{r}) + V_{\text{h}}(\mathbf{r})\right\} = \frac{1}{2}\left\{\tilde{V}_{\text{nuc}}(\mathbf{r}) + \tilde{V}_{\text{h}}(\mathbf{r}) + V_{\text{crc}}(\mathbf{r})\right\},\tag{s-28}$$

where  $\tilde{V}_{\text{nuc}}(\mathbf{r}) + \tilde{V}_{\text{h}}(\mathbf{r})$  is the electrostatic potential with a compensating background charge, and  $V_{\text{crc}}(\mathbf{r})$  is the correction for finite charge systems.  $V_{\text{crc}}(\mathbf{r})$  in the range of  $0 \le z \le L_z$  is given by

$$V_{\rm crc}(\mathbf{r}) = -2\pi \frac{\Delta Q}{SL_z} \left( z^2 + 2z'_0 z \right) + C, \qquad (s-29)$$

where C and an arbitrary constant,  $0 \le z \le L_z$  is the range of the simulation box along the z-direction,  $SL_z$  is the cell volume, and  $z'_0$  is a constant position parameter used to define a common reference point for the electrostatic potential.  $z'_0$  is defined as  $z'_0 = z_{\rm ref} - L_z/2$ , where  $L_z/2$  is half the box length and the electrostatic potential has the reference value of 0 at  $z_{\rm ref}$ ; thus,  $z'_0$  can be regarded as the central position of the charged layer (further details of  $z'_0$  and  $z_{\rm ref}$  are given below).  $\Delta Q$  in Eq. (s-29) is the total charge of the system given by

$$\Delta Q = \int \left\{ \rho(\mathbf{r}) + \sum_{\text{nuc}} \delta(\mathbf{r} - \mathbf{r}_{\text{nuc}}) Z_{\text{nuc}}(\mathbf{r}) \right\} d\mathbf{r}.$$
 (s-30)

 $E_{\rm es}$  is then given by

$$E_{\rm es} = \int \frac{1}{2} \left\{ \tilde{V}_{\rm nuc}(\mathbf{r}) + \tilde{V}_{\rm h}(\mathbf{r}) + V_{\rm crc}(\mathbf{r}) \right\} \cdot \left\{ \rho(\mathbf{r}) + \sum_{\rm nuc} \delta(\mathbf{r} - \mathbf{r}_{\rm nuc}) Z_{\rm nuc}(\mathbf{r}) \right\} d\mathbf{r} + \frac{1}{2} C \Delta Q - \frac{1}{2} \sum_{\rm nuc} Z_{\rm nuc}^2 \frac{\alpha}{\sqrt{\pi}}.$$
(s-31)

Because of the periodic boundary condition, the calculated internal energy  $E_{\text{escal}}$  is not  $E_{\text{es}}$ and includes the contribution of the uniform background charge,

$$E_{\text{escal}} = \int \frac{1}{2} \left\{ \tilde{V}_{\text{nuc}}(\mathbf{r}) + \tilde{V}_{\text{h}}(\mathbf{r}) \right\} \cdot \left\{ \rho(\mathbf{r}) + \sum_{\text{nuc}} \delta(\mathbf{r} - \mathbf{r}_{\text{nuc}}) Z_{\text{nuc}}(\mathbf{r}) - \frac{\Delta Q}{SL_z} \right\} d\mathbf{r}$$
  
+ 
$$\frac{1}{2} C \Delta Q - \frac{1}{2} \sum_{\text{nuc}} Z_{\text{nuc}}^2 \frac{\alpha}{\sqrt{\pi}}.$$
(s-32)

Therefore,  $E_{\text{escal}}$  should be corrected to obtain  $E_{\text{es}}$  by adding the following term  $E_{\text{cor}}$ :

$$E_{\rm cor} = \int \frac{1}{2} V_{\rm crc}(\mathbf{r}) \cdot \left\{ \rho(\mathbf{r}) + \sum_{\rm nuc} \delta(\mathbf{r} - \mathbf{r}_{\rm nuc}) Z_{\rm nuc}(\mathbf{r}) \right\} d\mathbf{r} + \int \frac{1}{2} \left\{ \tilde{V}_{\rm nuc}(\mathbf{r}) + \tilde{V}_{\rm h}(\mathbf{r}) \right\} \cdot \frac{\Delta Q}{SL_z} d\mathbf{r}.$$
(s-33)

The C dependence in Eq. (s-31) is canceled out by the corresponding term in the solvation free energy (Eq. (s-10)),

$$\Delta \mu = \sum_{\gamma} \frac{\rho_{\gamma}}{\beta} \int \frac{1}{2} \{h_{\gamma}(\mathbf{r})\}^{2} \Theta \left(-h_{\gamma}(\mathbf{r})\right) - \{c_{\gamma}'(\mathbf{r}) - \beta q_{\gamma}C\} + \frac{1}{2}h_{\gamma}(\mathbf{r}) \{c_{\gamma}'(\mathbf{r}) - \beta q_{\gamma}C\} d\mathbf{r}$$

$$= \sum_{\gamma} \frac{\rho_{\gamma}}{\beta} \int \frac{1}{2} \{h_{\gamma}(\mathbf{r})\}^{2} \Theta \left(-h_{\gamma}(\mathbf{r})\right) - c_{\gamma}'(\mathbf{r}) + \frac{1}{2}h_{\gamma}(\mathbf{r})c_{\gamma}'(\mathbf{r})d\mathbf{r}$$

$$-\frac{1}{2}C\Delta Q, \qquad (s-34)$$

where  $c_{\gamma}(\mathbf{r})$  is rewritten as  $c'_{\gamma}(\mathbf{r}) - \beta q_{\gamma}C$ , and the electroneutrality of the total system,

$$\Delta Q + \sum_{\gamma} q_{\gamma} \rho_{\gamma} \int h_{\gamma}(\mathbf{r}) d\mathbf{r} = 0, \qquad (s-35)$$

is applied. The last term of Eq. (s-34) is canceled out by the corresponding term in Eq. (s-31). Therefore, the total free energy does not depends on the parameter C. An analogous cancellation is satisfied in the effective screening medium (ESM)-RISM method.<sup>12</sup>

In the practical computation, the parameter C is defined so that the electrostatic potential generated by the charged layer is 0 at the reference position  $z_{\rm ref}$ . The total electrostatic potential shift by the charged layer is proportional to half of the box length,  $L_z/2$ . Thus, the box length determines the distance between the reference position  $z_{\rm ref}$  and the charged layer position ( $z_0$  and  $z'_0$ ). Therefore, the values of  $z_0$ ,  $z'_0$ , and  $z_{\rm ref}$  can be rationally defined. For example, in this study,  $z_0$  and  $z'_0$  were set to 79 Å because the surface Pt layer is at z =79 Å, and the box length is 144 Å. Then, the reference position should be defined as  $z_{\rm ref} \equiv$ 79 Å - 144/2 Å = 7 Å. When the distance between the reference position and the charged layer position is fixed, changing their positions results in dipolar electrostatic potential shift. As the positions of  $z_0$  and  $z'_0$  are apart from the real central position of the charged layer, the artificial dipolar interaction contributes to the total energy. However, the artificial interaction becomes small as the box size increases, and thus, has a minor contribution to the total energy when the box size is sufficiently large. Indeed, it is included in our case study.

Another correction method such as the Lagrange multiplier technique<sup>13,14</sup> would be also used for the SALMON program. However, the present equation is derived by simply rewriting the equation of the total energy for the semi-infinite electrode system. Indeed, the uniform background correction is only made to the total energy, not to the Kohn-Sham equation. Accordingly, the corrections have no effect on the wave function and liquid structure. Therefore, we selected the uniform background correction because its simplicity enables to retain unchanged the original part of the SALMON program.

#### S2 Standard Hydrogen Electrode Potential

The calculated reaction free energy of  $2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2$  in 1.0 M HClO<sub>4</sub> aqueous solution is -5.40 eV, from which the standard hydrogen electrode (SHE) potential was given as 5.40 V in this study. The calculated SHE potential is slightly higher than the experimental estimation of 4.44 V.<sup>15</sup> This is simply due to the definition of the potential. To be precise, the computational SHE was different from the true SHE because of the watervacuum surface potential  $\chi$ .<sup>16,17</sup> The SHE value references the absolute potential against the vacuum while we evaluated the value against the solution. Therefore, the computational SHE value is different because of the water-vacuum surface potential, which was reported to be 1.1-1.4V.<sup>18</sup> The computed SHE becomes in closer agreement with experimental values by considering the surface potential. The contribution of  $\chi$  is cancelled out in the evaluation of the relative free energy as we also did not correct the electrode potential using  $\chi$ .<sup>19</sup> In fact, using this computational SHE value, the pzc of  $Pt_{noad}$  surrounded by 1.0 M HClO<sub>4</sub> aqueous solution was calculated to be 0.53 V vs. SHE, which are qualitatively in agreement with previous experimental and theoretical values for a Pt electrode surrounded by an aqueous solution (0.23–0.56 V vs. SHE or the normal hydrogen electrode potential (NHE)).<sup>18,20–25</sup> The calculated reaction free energy of  $4H_3O^+ + O_2 + 4e^- \rightarrow 6H_2O$  at the computational SHE is 2.55 eV, which is also in agreement with the experimental value of 2.46 eV.  $^{26}$  The error cancellation contributes to the accordance of the reaction free energy. The water formation energy is underestimated by  $\sim 0.2 \text{ eV}$  per H<sub>2</sub>O molecule using the PBE functional.<sup>27</sup> Meanwhile, the thermodynamic corrections were not applied in this study, leading to the overestimation of the reaction energy of  $H_2 + 1/2 O_2 \rightarrow H_2O$  by  $\sim 0.3 \text{ eV}$ .<sup>28</sup> Consequently, these opposing errors effectively cancel each other out.

#### S3 Free Energy Calculation of Charged Molecule

In Sec. S2, we utilized the standard 3D-RISM-SCF method for H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> under the periodic boundary condition, where the finite charge correction was not applied. The energy error for a charged molecule is approximately inversely proportional to the box length,  $L_{\rm box}$ , when the periodic boundary condition is applied and the box shape is cubic.<sup>29,30</sup> In Figure S1,  $E_{\rm ele}$  and  $\Delta\mu$  of H<sub>3</sub>O<sup>+</sup> are plotted against the inverse box size,  $L_{\rm box}^{-1}$ , where the box size was set to  $L_{\rm box}^3$  and the box has the cubic shape.  $E_{\rm ele}$  and  $\Delta\mu$  have the negative and positive slopes with respect to  $L_{\rm box}^{-1}$ , respectively. Their dependences on the box size are almost canceled out with each other. This is reasonable because the 3D-RISM-SCF method is based on the grand canonical framework and thus the total system consisting of the solute and solvent is charge neutral. The y-intercepts for  $E_{\rm ele}$  and  $\Delta\mu$ , which correspond to their limiting values at  $L_{\rm box} \to \infty$ , are estimated to be -475.11 eV and -3.11 eV using the least square fitting. The free energy at  $L_{\rm box} \to \infty$  is then estimated to be -478.23 eV, which is only 0.03 eV smaller than the result of  $L_{\rm box} = 40$  Å ( $L_{\rm box}^{-1} = 0.025$  Å<sup>-1</sup>) used in this study.

Figure S2 presents the 3D density distributions and their corresponding cross sections for the O site of H<sub>2</sub>O (O<sub>w</sub>), O site of H<sub>3</sub>O<sup>+</sup> (O<sub>c</sub>), and O site of  $\text{ClO}_4^-$  (O<sub>a</sub>) around H<sub>3</sub>O<sup>+</sup> when the box size is  $L_{\text{box}} = 40$  Å. The cross sections are obtained by cutting through the O atom position of H<sub>3</sub>O<sup>+</sup>. As seen from Figure S2, the distributions converged to the average value of 1, indicating that the box size is sufficiently large.



Figure S1: Dependence on the inverse box size  $L_{\text{box}}^{-1}$  for the free energy of H<sub>3</sub>O<sup>+</sup> in 1.0 M HClO<sub>4</sub> aqueous solution.



Figure S2: 3D density distributions and their cross sections of 3D density distributions of the  $HClO_4$  aqueous solution around  $H_3O^+$  for (a, b)  $O_w$ , (c, d)  $O_c$ , and (e, f)  $O_a$ . The distribution less than 0.001 is not shown in the cross sections for the visibility.

## S4 Dependence of Free Energy Profile on Concentration

Figure S3 shows the free energy profiles using 1.0 M and 0.2 M HClO<sub>4</sub> aqueous solution. The result for the 1.0 M solution is the same as that shown in the main manuscript. We corrected the free energy of  $H_3O^+$  by adding the entropic contribution depending on the concentration,  $k_B T \ln[H_3O^+]$ .<sup>28</sup> Here, the solvation free energies of H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> in the 0.2 M homogeneous solution were assumed to be the same as those in the 1.0 M solution because we focused on the EDL structure change depending on the concentration. The present result shows that the difference in the energy profile at the pzc between the 0.2 M solution and the 1.0 M solution is primarily due to variation in the electrode potential and the proton or  $[H_3O^+]$  concentration,  $k_BT\ln[H_3O^+]$ . The difference in  $k_BT\ln[H_3O^+]$  of the 0.2 M solution from that of the 1.0 M solution is 0.08 eV for the  $Pt_{noad}$  and  $Pt-O_{ad}$  states and 0.04 eV for the Pt-OH<sub>ad</sub> states, respectively. The electrode potentials at the pzc are 0.53 V for 1.0 M solution and 0.62 V for 0.2 M solution, respectively. Consequently, the energy difference owing to the electrode potential is 0.18 eV for the  $Pt_{noad}$  and  $Pt-O_{ad}$  states and 0.09 eV for the Pt-OH<sub>ad</sub> state, respectively. Therefore, the differences other than the [H<sub>3</sub>O<sup>+</sup>] concentration and the electrode potential contribute to the stability only by 0.03 eV for the  $Pt-O_{ad}$  state and 0.05 eV for the  $Pt-OH_{ad}$  state at the pzc.

The energy differences from the pzc to 0.90 V (depicted by the dark blue-red arrows in Fig. S3) are 0.55 eV for the Pt-O<sub>ad</sub> state and 0.30 eV for the Pt-OH<sub>ad</sub> state, when the 0.2 M solution was used. These values are also in agreement with the simple estimation based on the classical electrochemistry used in the CHE model,  $\Delta Q_{\text{tot}} \cdot U_{\text{pot}}$  (see the main manuscript for details), 0.56 eV for the Pt-O<sub>ad</sub> states and 0.28 eV for the Pt-OH<sub>ad</sub> state. These results indicate that the EDL formation has a negligible influence on Pt-O<sub>ad</sub> and Pt-OH<sub>ad</sub>, when the 0.2 M solution is used.



Figure S3: Free energy profiles of the oxygen reduction reaction at the potential of zero charge (pzc) of  $Pt_{noad}$  and at 0.90 V relative to the standard hydrogen electrode potential (SHE).

#### S5 Solvation Structure

Figures S4 and S5 show the average density distributions of the 1.0 M HClO<sub>4</sub> solution along the z-axis perpendicular to the Pt surface at 0.53 V (the pzc of Pt<sub>noad</sub>) and 0.90 V relative to the standard hydrogen electrode (SHE) potential. The results for the O site of  $ClO_4^-$  (O<sub>a</sub>) and H site of H<sub>3</sub>O<sup>+</sup> (H<sub>c</sub>) are shown in Figure S4, and those for the O and H sites of H<sub>2</sub>O (O<sub>w</sub> and H<sub>w</sub>) are shown in Figure S5.

To compare the magnitudes of the  $\text{ClO}_4^-$  and  $\text{H}_3\text{O}^+$  densities around the adsorbates, the 3D density distribution at 0.90 V using a different threshold for  $g(\mathbf{r})$  from that in the main manuscript is shown in Figure S6. In addition, the cross sections of 3D density distributions of  $\text{Cl}_a$ ,  $\text{O}_a$ , and  $\text{O}_c$  at 0.90 V are shown in Figure S7. Figures S8 and S9 shows the 3D density distribution of O of H<sub>2</sub>O, H of H<sub>2</sub>O, and H of H<sub>3</sub>O<sup>+</sup> at the PZC potential and 0.8 V, respectively.



Figure S4: Density distributions of ions in the  $\text{HClO}_4$  aqueous solution perpendicular to the Pt surface,  $g(z) = \frac{1}{S} \int g(\mathbf{r}) dx dy$ , near  $\text{Pt}_{\text{noad}}$  (black), Pt-O<sub>ad</sub> (blue), and Pt-OH<sub>ad</sub> (red) at (a) 0.53 V and (b) 0.90 V.



Figure S5: Density distributions of water in the HClO<sub>4</sub> aqueous solution perpendicular to the Pt surface,  $g(z) = \frac{1}{S} \int g(\mathbf{r}) dx dy$ , near Pt<sub>noad</sub> (black), Pt-O<sub>ad</sub> (blue), and Pt-OH<sub>ad</sub> (red) at (a) 0.53 V and (b) 0.90 V.



Figure S6: 3D density distributions of the  $\rm HClO_4$  aqueous solution for  $\rm Pt\text{-}O_{ad}$  (left) and  $\rm Pt\text{-}OH_{ad}$  (right).



Figure S7: Cross section of 3D density distributions of the  $HClO_4$  aqueous solution for Pt- $O_{ad}$  (left) and Pt- $OH_{ad}$  (right) at 0.90 V of  $Cl_a$  (a and b),  $O_a$  (c and d) and  $O_c$  (e and f).



Figure S8: 3D density distributions of the  $\rm HClO_4$  aqueous solution for  $\rm Pt-O_{ad}$  (left) and  $\rm Pt-OH_{ad}$  (right) at the PZC potential.



Figure S9: 3D density distributions of the  $\rm HClO_4$  aqueous solution for  $\rm Pt-O_{ad}$  (left) and  $\rm Pt-OH_{ad}$  (right) at 0.8 V.

#### S6 Solvation Structure of 0.2 M HClO<sub>4</sub> solution

Figure S10 shows the average density distributions of the  $0.2 \text{ M HClO}_4$  solution along the *z*-axis perpendicular to the Pt surface. The density distribution of ions becomes broaden along the *z*-direction relative to that for the 1.0 M solution, indicating that the short-range interaction between the adsorbates and solution becomes weaker as the concentration decreases. It is noted that the value of the distribution function is the ratio relative to the average concentration. For example, when the value of the distribution function is the same, the number of the ions of 0.2 M solution is smaller by 5 times than that of the 1.0 M solution.



Figure S10: Density distributions of the 0.2 M HClO<sub>4</sub> aqueous solution perpendicular to the Pt surface,  $g(z) = \frac{1}{S} \int g(\mathbf{r}) dx dy$ , near Pt<sub>noad</sub> (black), Pt-O<sub>ad</sub> (blue), and Pt-OH<sub>ad</sub> (red) at 0.90 V.

#### S7 Electrostatic Potential Distribution

Figure S11 shows the cross section of the change in the electrostatic potential  $(V_{ps}(\mathbf{r}) + V_{h}(\mathbf{r}) + V_{sol}(\mathbf{r}))$  due to a 0.37 V increase in the electric potential when 1.0 M HClO<sub>4</sub> aqueous solution is used. The range of the color gradient is set to be smaller than that given in the main manuscript.



Figure S11: Cross section of the change in the electrostatic potential due to a 0.37 V increase relative to the potential of zero charge (pzc) for (a)  $Pt_{noad}$ , (b)  $Pt-O_{ad}$ , and (c)  $Pt-OH_{ad}$  surrounded by 1.0 M HClO<sub>4</sub> solution. The color gradient ranges from -0.15 (blue) to +0.15 V (red). The position of the adsorbed O atom is marked with "+".

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