Usage Report for Fiscal Year 2019

Project Title:

Turning frustration into electrochemical CO_2 activation

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１． Background

Since Rosen et al. in 2011 found that imidazolium ionic liquid significantly increases the activity and selectivity of the electrochemical reduction of CO_2 to CO, the catalytic role of imidazolium ionic liquid in CO_2 reduction has been intensively investigated. To date, however, the molecular mechanism behind this activity and selectivity remains to be elucidated. In our previous calculation paper, which also used the calculation resource of HOKUSAI, the reduction potential of the 1-ethyl-3-methylimidazolium ($EMIM^+$) cation was estimated to be –2.4 V assuming a homogeneous reaction in the absence of electrode material. And it was proposed to be the key step of controlling CO_2 activation. To bridge the gap between experiments (–0.8 V) and calculation (–2.4 V), further theoretical calculations of the reduction potential of the $EMIM^+$ cation within the framework of an electrode effect is desired to examine the formation of EMIM radical.

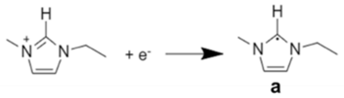
２． Methods

To simulate the presence of the copper electrode, the Cu(111) surface was modeled by a periodically repeating 3×3 supercell in a three-layer slab determined with plane-wave-based DFT calculations. Copper atoms in the second and third layers were fixed, whereas copper atoms in the first layer were allowed to relax. The calculations were carried out using Perdew-Burke-Ernzerhof (PBE) functional and ultrasoft pseudopotentials as implemented in Quantum Espresso code. The plane wave kinetic energy cut off values of 40 and 480 Ry were adopted for the wave functions and charge densities, respectively. The Monkhorst-Pack type of k-point sampling with an 8×8×1 choice was selected for the slab calculations. The Brillouin zone was integrated using the Methfessel-Paxton smearing method. Finally, Grimme D2 dispersion and dipole corrections (in the presence of Cu(111) and imidazolium species) were applied.

The cluster model of imidazolium species and 18 or 4 copper atoms was calculated using PBE functional as implemented in Gaussian 09. LANL2DZ was adopted for copper atoms and 6-311++G(d,p) for the other atoms. The SMD solvation model was adopted to account for the solvation effect on the cluster model. The D3 version of Grimme's dispersion with Becke-Johnson damping was used to account for dispersion. Raman spectra of $EMIM^+$ cations and EMIM radicals without copper atoms included were calculated using B3LYP functional and 6-311++G(d,p) basis set in the PCM solvation model as implemented in Gaussian 09. A scaling factor of 0.967 for frequency correction was adopted.

３． Results

To understand the potential dependent Raman spectra associated with $EMIM^+$ cations, six possible species previously proposed as in-situ generated $EMIM^+$ cations derivatives during electrochemical CO_2 reduction were calculated as shown in equations below.



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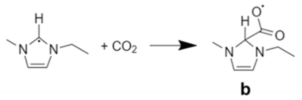

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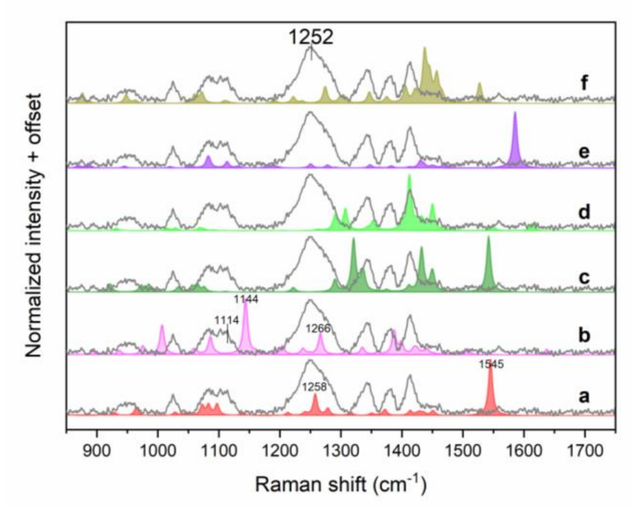
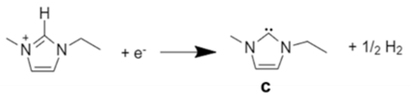


Figure 1. Calculated Raman spectra of possible species **a**, **b**, **c**, **d**, **e** and **f** as shown from Eq. (1) to (6). Grey curves represent experimental Raman spectrum recorded at –1.0 V.



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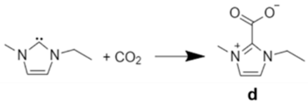

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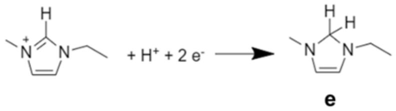

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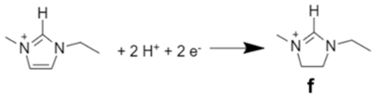
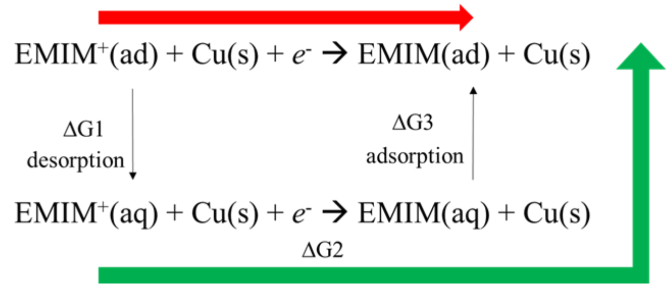


(6)

Fig. 1 shows the comparison of experimentally observed Raman spectrum at –1.0 V with calculated ones of these species. It can been seen that the main features of intense bands appearing at around 1252 cm^{-1} together with disappearance of the bands at around 1450 cm^{-1} at lower potential than –0.8 V can be well represented by the calculated Raman spectrum of EMIM radical (species **a**) and its derivative **b**. However, there is a very strong band (1545 cm^{-1}) from calculated Raman spectrum of species **a** which was missing in the experimental one. Thus species **b** contributed to the main feature in the observed Raman spectra at around 1252 cm^{-1} which is assigned as O-C-O bending vibration coupled with C2-H bending.

As direct calculation of the reduction potential is challenging, here, we adopted the strategy used by Ertem et al. to set up a thermodynamic cycle (Scheme 1). The free energy change from adsorbed $EMIM^+$ cation to adsorbed EMIM radical (denoted as ΔG) can be separated into three terms: (i) desorption of adsorbed $EMIM^+$ cation on the Cu(111) surface (ΔG_1); (ii) reduction of aqueous $EMIM^+$ cation to aqueous EMIM radical (ΔG_2); and (iii) adsorption of aqueous EMIM radical on the Cu(111) surface (ΔG_3). ΔG_2 was previously estimated to be –43.6 kcal/mol (corresponds to –2.4 V) based on cluster DFT calculations.



Scheme 1. Thermodynamic cycle used for calculation of the standard reduction potential of the EMIM+ cation.

ΔG_1 and ΔG_3 can be approximated as the sum of the three terms:

$$\Delta G = \Delta E + \Delta G_{corr} + \Delta G_{solv} \quad (7)$$

where ΔE is the difference of electronic energies of the optimized structures obtained via plane-wave-based DFT calculations; ΔG_{corr} is the difference of the thermal correction to free energy calculated by cluster DFT calculations employing the standard ideal-gas, rigid-rotator, harmonic oscillator approximation; ΔG_{solv} is the solvation energy difference within the SMD model via cluster DFT calculations. Especially, $EMIM\text{-}BF_4$ (with counter anion) was used in calculating desorption free energy of adsorbed $EMIM^+$ cation to make the system neutral. Fig. 2 shows the geometric structures of adsorbed EMIM radical and $EMIM^+$ cation on the Cu(111) surface. Using Eq. 7, desorption free energy ΔG_1 and adsorption free energy ΔG_3 were calculated to be 59.7 and –39.6 kcal/mol, respectively. Therefore, the corrected reduction potential from adsorbed

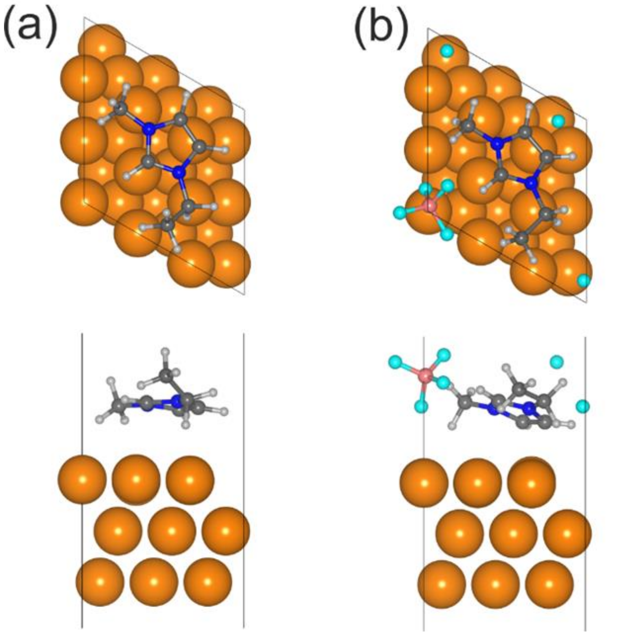


Figure 2. Top view (upper) and side view (bottom) of adsorbed EMIM radical (a) and adsorbed $EMIM^+$ cation (b) on the Cu(111) surface. Orange spheres represent Cu atoms and C, N, H, B and F atoms are shown by grey, blue, light grey, pink and turquoise colors, respectively.

$EMIM^+$ cation to EMIM radical (denoted in red curve in Scheme 1) was estimated to be –3.3 V, a value that is more negative than –2.4 V. However, if we consider the reduction potential from aqueous $EMIM^+$ cation to adsorbed EMIM radical (denoted in green curve in Scheme 1), the value was shifted to –0.7 V, which is in good agreement with the obtained experimental value of ~–0.8 V. This result indicated that the reduction of aqueous $EMIM^+$ cation to adsorbed EMIM radical is energetically feasible under onset potential of CO_2 reduction.

4. Conclusion

DFT calculation showed that the reduction from aqueous $EMIM^+$ cation to adsorbed EMIM radical on Cu(111) occurs at –0.7 V. The coincidence of $EMIM^+$ cations reduction potential (–0.7 V determined by DFT calculation) and onset of CO_2 reduction (–0.89 V determined by cyclic voltammetry and ~–0.8 V by on-line differential electrochemical mass spectrometry) strongly suggests that a reduced $EMIM^+$ cation species initiates CO_2 reduction.

5. Schedule and prospect for the future

None.

6. If no job was executed, specify the reason.

HOKUSAI calculation source was mainly used to analyze the previous calculation results obtained from HOKUSAI calculation system.

Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

[1] Wang, Yuanqing, Toru Hayashi, Daoping He, Yamei Li, Fangming Jin, and Ryuhei Nakamura. A reduced imidazolium cation layer serves as the active site for electrochemical carbon dioxide reduction. Applied Catalysis B: Environmental 264 (2020): 118495.

[Conference Proceedings]

[Oral presentation]

[Poster presentation]

[Others (Book, Press release, etc.)]