A Lattice-Oxygen-Involved Reaction Pathway to Boost Urea Oxidation

Longsheng Zhang*, Liping Wang*, Haiping Lin*, Yunxia Liu, Jinyu Ye, Yunzhou Wen, Ao Chen, Lie Wang, Fenglou Ni, Zhiyou Zhou, Shigang Sun, Youyong Li, Bo Zhang,* and Huisheng Peng*

Abstract: The electrocatalytic urea oxidation reaction (UOR) provides more economic electrons than water oxidation for various renewable energy-related systems owing to its lower thermodynamic barriers. However, it is limited by sluggish reaction kinetics, especially by CO_2 desorption steps, masking its energetic advantage compared with water oxidation. Now, a lattice-oxygen-involved UOR mechanism on Ni^{4+} active sites is reported that has significantly faster reaction kinetics than the conventional UOR mechanisms. Combined DFT, 18O isotope-labeling mass spectrometry, and in situ IR spectroscopy show that lattice oxygen is directly involved in transforming *CO to CO_2 and accelerating the UOR rate. The resultant Ni^{4+} catalyst on a glassy carbon electrode exhibits a high current density (264 mACm^-2 at 1.6 V versus RHE), outperforming the state-of-the-art catalysts, and the turnover frequency of Ni^{4+} active sites towards UOR is 5 times higher than that of Ni^{3+} active sites.

The urea oxidation reaction (UOR) is known as a central chemical reaction in the area of energy storage, urea fuel cells, de-ureation of wastewater, artificial kidneys, and so on. Especially in the application of clean energy conversion and storage, UOR can work as an alternative anodic reaction to oxygen evolution reaction (OER), which provides electrons for hydrogen evolution, CO_2 reduction, and N_2 reduction reactions. Notably, an electrolytic cell potential of 0.37 V is thermodynamically required to electrolyze urea at standard conditions, which is much lower than the 1.23 V required to electrolyze water theoretically.[5] Besides, UOR utilizes urea from abundant wastewater, offering a means to develop renewable alternative energy sources and treat wastewater simultaneously. It is estimated that over 2200 billion tons of wastewater is produced globally in 2010, and around 80% of which is discharged directly into rivers, lakes, and oceans.[6]

However, urea electrolysis suffers from intrinsically sluggish kinetics owing to its 6e^- transfer process, complicated intermediates transfer, and multiple gas-desorption steps.[7] Previous studies showed that nickel oxides exhibited higher catalytic activity for UOR than other metals and metal oxides in alkaline media,[8–10] where Ni^{3+} sites were identified as the catalytic active sites.[11] The typical reaction pathway was proposed as: *CO(NH_2)_2 → *CO(NH(NH_2)) → *CO(NH(NH_C_2H_5)) → *CO(NH(NH_C_2H_5)_2) → *CO(NH(NH_C_2H_5)_2) → *CO(OH) → *COO, with the desorption of *COO intermediate as the rate-determining step (RDS). [11] Various approaches including surface engineering,[12] structural distortion,[13] and element doping[14] were explored to modulate the electronic structures of Ni^{4+} active sites and enhance their density in catalysts for better urea electrolysis. Unfortunately, these UOR catalysts still exhibit unsatisfactory catalytic activity, owing to the unfavorably strong binding of Ni^{3+} active sites with *COO intermediate. Breakthroughs in developing high-performance electrocatalysts with lower energy barrier for *COO intermediate desorption are urgently desired.

Metal-oxygen hybridization in electrocatalysts was found to correlate with enhanced electrochemical reaction kinetics, where the increased covalence of metal-oxygen bonds is critical to activate the lattice oxygen and promote new reaction pathways.[15–17] It has been noted from theory and experimental studies that high-valence transition-metal sites with a low energy metal 3d state can enhance metal–oxygen hybridization owing to the shortened energy distance between the metal 3d and oxygen 2p band centers.[18] We posit that modulating the oxidation state of Ni active sites and the ensuing enhanced Ni–O covalency, may trigger the activation of lattice oxygen to couple with the *CO intermediate, and therefore may facilitate *COO intermediate desorption, the RDS of UOR.

Herein, we further develop the physical model and explore the reaction pathway of UOR with respect to the oxidation states of Ni active sites. Using density functional theory (DFT) calculations, we find that lattice-oxygen-involved reaction pathway of UOR is preferred energetically.

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State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University
Shanghai, 200438 (China)
E-mail: bozhang@fudan.edu.cn penghs@fudan.edu.cn
Prof. H. Lin, Y. Liu, Prof. Y. Li
Institute of Functional Nano & Soft Materials (FUNSOM) and Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University
Suzhou, 215123 (China)
E-mail: yyl@suda.edu.cn
J. Ye, Prof. Z. Zhou, Prof. S. Sun
State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University
Xiamen, 361005 (China)

[2] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
on the Ni\(^{3+}\) active sites, which has significantly faster reaction kinetics than the conventional reaction pathway occurred on Ni\(^{3+}\) active sites. To experimentally verify the calculations, we synthesized Ni\(^{2+}\) and Ni\(^{3+}\) oxides, as confirmed by in situ X-ray absorption fine structure (XAFS) spectroscopy and quasi in situ soft X-ray absorption spectroscopy (sXAS). The isotope-labeling secondary-ion mass spectrometry (SIMS), combined with in situ Fourier transform infrared (FTIR) spectroscopy, provides solid evidence for the involvement of lattice oxygen during UOR. The electrochemical results show that the turnover frequency (TOF) of Ni\(^{4+}\) active sites towards UOR is 5 times higher than that of Ni\(^{3+}\) active sites.

Spin-polarized DFT calculations were employed to investigate the reaction pathways of the UOR on the conventional Ni\(^{3+}\) active sites and Ni active sites with higher oxidation states. The computational methods and the structural details of slab models are described in the Supporting Information. The Ni\(^{3+}\) sites are regarded as the active sites in the NiOOH surface. By removing the top layer of H atoms in the NiOOH surface, we obtain the NiOO surface. The Bader charge analysis shows that the oxidation states of Ni sites in the NiOO surface are higher than the Ni sites in the NiOOH surface (Supporting Information, Figure S1). The covalence of Ni–O bonds in the NiOO and NiOOH surfaces is further investigated by the projected densities of states (PDOS). As shown in the Supporting Information, Figure S2, the hybridization between the Ni states and O states is more profound in the NiOO surface than that in the NiOOH surface, suggesting that Ni–O bonds in the NiOO surface possess a more covalent bonding character than that in the NiOOH surface. According to the previous studies, the activity of lattice oxygen atoms increases with increasing covalency of metal–oxygen bonds. To confirm this, the formation energies of oxygen vacancies are calculated for these two surfaces. As shown in the Supporting Information, Figure S3, the energy penalty for producing an oxygen vacancy in the NiOO surface (1.69 eV) is indeed lower than that of NiOOH surface (2.61 eV), indicating that the lattice oxygen atoms in the NiOO surface are more active than those of NiOOH surface and thus more likely to get involved in the UOR. Based on such an assumption, the energy profiles of two UOR paths are calculated. As seen in Figure 1, the lattice oxygen atoms in the NiOOH surface do not involve in the reactions. While on the NiOO surface, the lattice oxygen atoms react with the \(\text{CONNH}_2\) intermediate to form line-type adsorbed CO\(_2\) molecules, which may readily desorb from the surface of catalyst. As a result, on the NiOOH surface, the last step of CO\(_2\) desorption exhibits a potential-independent energy barrier of 0.90 eV. It is noted that the adsorption energy of a urea molecule on two adjacent Ni\(^{3+}\) ions on the NiOOH surface is \(-1.79\) eV, which is similar to the binding energy of two CO\(_2\) molecules on two Ni\(^{3+}\) ions \((-0.90 \times 2 = -1.80\) eV). This strongly implies that the CO\(_2\) desorption and the subsequent re-generation of Ni\(^{3+}\) active sites may be a slow process in the catalytic cycle. Previous investigations also ascribed the experimentally observed RDS of UOR on NiOOH to the CO\(_2\) desorption, which agrees well with our computational results.

On the NiOO surface, the formation of CO\(_2\) occurs before that of N\(_2\), owing to the coupling between lattice oxygen atoms and the \(\text{CONNH}_2\) intermediate. As a result, CO\(_2\) desorption on the NiOO surface is observed to take place upon structural relaxations, indicating that it is a fast and spontaneous process. Furthermore, potential-independent step of water desorption from the NiOO surface has a low energy barrier of only 0.27 eV, revealing that the re-generation of active sites is very feasible. Taking into account the fact that most electrocatalytic UOR potentials on the NiOO surface are lower than those on the NiOOH surface, the NiOO surface is regarded as a more active catalyst. The key characteristic of the NiOO catalyzed UOR path is the activation of lattice oxygen atoms, which reduces not only the electrocatalytic potentials, but also the energy barriers of the potential-independent re-generations of the active sites.

One of the most direct approaches to obtain the NiOO surfaces is to replace the surface hydroxyl groups of Ni(OH)\(_2\) with O atoms. DFT calculations show that this is an endothermic process with an energy increase of 0.56 eV per O site. Starting from the nickel hydroxycarbonate (noted as NiClOH), however, the NiOO surface can be produced by...
replacing Cl and OH groups with O atoms. Such a process is also endothermic, but the energy increase per O site is only 0.18 eV. This strongly implies that the NiOO surfaces are more likely to be produced from NiClOH than from Ni(OH)$_2$ (Figure 2a).

Inspired by DFT calculation results, we first prepared NiClOH nanosheets and pristine Ni(OH)$_2$ nanosheets as control (Supporting Information, Figure S4; see synthesis details in Supporting Information). Transmission electron microscopy and corresponding energy dispersive spectroscopy in the Supporting Information, Figure S5 reveals the homogeneous distribution of chlorine within the as-prepared NiClOH nanosheet. All of the chlorine leached out into the electrolyte during the electrochemical oxidation of NiClOH sample, as verified by the high-resolution Cl 1s spectra of X-ray photoelectron spectroscopy (Supporting Information, Figure S6). After electrochemical oxidation, the NiClOH sample turns into smaller nanosheets with lateral sizes at a range of 3–5 nm (Supporting Information, Figure S7). The Ni(OH)$_2$ sample after the same electrochemical oxidation features a nanosheet morphology with lateral sizes of 2–3 nm (Supporting Information, Figure S8). It is reported that structural defects (nickel vacancies) were generated during the preparation of the NiClOH sample, which would lead to new defect levels in the band gap and improved carrier density, thus enhancing the charge transport property and catalytic activity of UOR catalysts.$^{[3]}$ For simplicity, the as-formed samples after electrochemical oxidation of NiClOH and Ni(OH)$_2$ nanosheets are denoted as NiClOH-derived catalyst (NiClO-D) and Ni(OH)$_2$-derived catalyst (NiOH-D), respectively. Accordingly, the as-formed samples after electrochemical oxidation of CoClOH and Co(OH)$_2$ are denoted as CoClO-D and CoOH-D catalysts, respectively.

We carried out in situ XAFS spectroscopy to probe the electronic structure of NiOH-D and NiClO-D samples. Figure 2b shows the Ni K-edge X-ray absorption near-edge structure (XANES) spectra of NiOH-D and NiClO-D, as well as commercial Ni, Ni(OH)$_2$, and Ni$_2$O$_3$ samples for reference. The XANES spectra of NiOH-D and Ni$_2$O$_3$ samples reveal that Ni$^{3+}$ remains the dominant valence state of NiOH-D. Comparatively, the shift of absorption threshold to higher energy for NiClO-D sample suggests that higher-valence nickel sites are formed in the NiClO-D. The Fourier transform $k^2$-weighted XAFS $\chi$ versus reciprocal wave vector (Supporting Information, Figure S9) indicates good qualities of all the data. The corresponding extended X-ray absorption

![Figure 2](image-url)

Figure 2. a) The formation energy from Ni(OH)$_2$ and NiClOH to NiOO models. b),c) Ni K-edge XANES and EXAFS spectra of NiOH-D, NiClO-D, commercial Ni, NiO, and Ni$_2$O$_3$ samples, respectively. Black circle are fitting curves, and the fill areas are Ni–Ni bonds for Ni$^{4+}$ (pink) and Ni$^{3+}$ (cyan). d) Ni L-edge sXAS spectra of NiOH-D, NiClO-D, and theoretical Ni$^{4+}$. 
fine structure (EXAFS) spectra of NiOH-D and NiClO-D are given in Figure 2c. By fitting their EXAFS spectra with the window from 1 to 4 Å (Supporting Information, Table S1), we observe two different peaks located at 2.89 Å and 3.15 Å for the NiClO-D sample, which are assigned to Ni–Ni bond distances of Ni\(^{4+}\) and Ni\(^{3+}\) sites, respectively. The molar ratio of Ni\(^{4+}\) and Ni\(^{3+}\) sites in the NiClO-D sample is around 3/2. There is one Ni–Ni bond distance of 3.12 Å for the NiOH-D sample, which is ascribed to Ni\(^{3+}\) sites, in agreement with the XANES results.

We further measured the Ni L-edge XAS spectroscopy by recording the total electron yield intensity (Figure 2d). We observe a peak located at 858.3 eV (indexed as Peak B) for the NiClO-D sample, which features a small but reproducible positive energy shift (ca. 0.2 eV) compared with that of NiOH-D sample, indicating the formation of Ni\(^{4+}\) sites in the NiClO-D sample, according to the theoretical Ni\(^{4+}\) spectrum. Besides, the peak at 856.0 eV (indexed as Peak A) in the NiOH-D sample is much stronger than that of NiClO-D sample. The intensity ratio of Peak B to A for NiClO-D is much higher than that of NiOH-D (as summarized in the Supporting Information, Table S2), which represents the increase of unoccupied states in 3d orbitals, suggesting its higher oxidation state. Notably, the intensity of peak located at 875.1 eV for the NiClO-D is appreciably stronger than that of NiOH-D, which also confirms the generation of Ni\(^{4+}\) species in the NiClO-D sample.

To evaluate the UOR catalytic activity with respect to the effect of Ni\(^{4+}\) sites, we conducted the electrochemical measurement of NiClO-D and NiOH-D catalysts. Linear sweep voltammery (LSV) on glassy carbon electrodes (GCEs) were carried out in 1 M KOH aqueous electrolyte with 0.33 M urea. The NiClO-D electrode manifests appreciably improved UOR catalytic activity compared with NiOH-D electrode (Figure 3a; Supporting Information, Figure S10). Specifically, the NiClO-D electrode requires a potential of 1.386 V (vs. reversible hydrogen electrode, RHE) to drive a current density of 50 mA cm\(^{-2}\), which is 110 mV lower than that of NiOH-D electrode. Moreover, the NiClO-D electrode exhibits a greatly enhanced current density (264 mA cm\(^{-2}\)) than NiOH-D electrode (81 mA cm\(^{-2}\)) at 1.6 V (vs. RHE), which outperforms state-of-the-art UOR catalysts (Supporting Information, Table S3). As shown in Figure 3b, the Tafel slope of NiClO-D electrode (41 mV dec\(^{-1}\)) is lower than that of NiOH-D electrode (74 mV dec\(^{-1}\)), indicating its faster reaction kinetics. The enhanced reaction kinetics of NiClO-D catalyst could be partially ascribed to the accelerated charge transport derived from its structural defects. In parallel with NiClO-D and NiOH-D catalysts, we also conducted the electrochemical measurement of CoClO-D and CoOH-D catalysts. As shown in the Supporting Information, Figure S11, the CoClO-D electrode exhibits much higher UOR activity than the CoOH-D electrode, which may be resulted from the generation of Co\(^{4+}\) sites in CoClO-D catalyst, but further studies are needed.

To further investigate the intrinsic activity of NiClO-D and NiOH-D, we normalized the current density using the electrochemically active surface area (ECSA) obtained by the double-layer capacitance (\(C_{dl}\)) technique (Supporting Information, Figure S12). The \(C_{dl}\) of NiClO-D electrode is calculated to be 1.65 mF cm\(^{-2}\), which is 1.38 times higher than that of NiOH-D electrode. The specific activities (ECSA-normalized current density) and mass activities (Supporting Information, Figure S13 and Table S4) of the NiClO-D catalyst are 2.4 times and 3.3 times higher than those of NiOH-D catalyst at 1.6 V (vs. RHE). As shown in Figure 3c, the TOF evaluation reveals superior intrinsic activity of NiClO-D catalyst with TOF of 0.21 s\(^{-1}\), in comparison with that (0.04 s\(^{-1}\)) of NiOH-D catalyst. These results, taken together, indicate that the Ni\(^{4+}\) active sites exhibit higher intrinsic activity than Ni\(^{3+}\) active sites towards UOR.

Aside from intrinsic catalytic activity, stability is another crucial factor for UOR catalysts. In the galvanostatic experiment for NiClO-D electrode performed at a constant current density of 10 mA cm\(^{-2}\), no appreciable increases in potential are observed over 100 h (Figure 3d), indicating its good durability. We next assembled a two-electrode electrolyzer...
using NiClO-D as anode for UOR and commercial Pt/C catalyst as cathode for hydrogen evolution reaction (HER) in 1M KOH solution with 0.33 M urea. We achieved a 1.69 V cell voltage at 100 mA cm⁻² for the HER/UOR electrolyzer (Figure 3c; Supporting Information, Figure S14). In contrast, when we used IrO₂/C catalyst as anode for OER and commercial Pt/C catalyst as cathode for HER in 1M KOH solution, the cell voltage of HER/OER electrolyzer reached 2.28 V at 100 mA cm⁻², indicating less electrical energy is needed for the HER/UOR electrolyzer to produce a given amount of H₂. The new UOR catalysts in this work exhibit higher catalytic performance for urea electrolysis and provide more efficient hydrogen generation.

To verify whether lattice oxygen of NiClO-D was involved in UOR, we designed ¹⁸O isotope-labeling mass spectrometry. As illustrated in Figure 4a, in the lattice-oxygen-involved reaction pathway, the oxygen from the electrolyte would immigrate into the as-formed oxygen vacancy (Vo⁺) on the surface of catalyst. We employed SIMS to investigate the exchange of lattice oxygen with electrolytes during UOR. The NiClO-D and NiOH-D catalysts were first dispersed on carbon-paper electrodes and then held for 1h O₂-vacuum for 6h to remove adsorbed H₂¹⁸O. The depth profiles of ¹⁸O and ¹⁶O elements in both NiClO-D and NiOH-D catalysts were determined by SIMS, and the intensity ratio of ¹⁸O to ¹⁶O are shown in Figure 4b. The ¹⁶O/¹⁸O intensity ratio of NiClO-D and NiOH-D samples both drop a little in the sputter time of first 50s, since there are still adsorbed H₂¹⁸O left on the surface of samples. Nevertheless, the ¹⁸O/¹⁶O intensity ratio of NiClO-D catalyst is about 92% after the sputter time of 50s, which is appreciably higher than that (7%) of NiOH-D catalyst. These results, taken together, provide experimental evidence for preferred lattice-oxygen-involved reaction pathway of NiClO-D catalyst in UOR.

To gain more insights into the UOR mechanism, in situ FTIR spectroscopy were carried out (Figure 4c and d). Both of the NiClO-D and NiOH-D catalysts exhibit a vibration peak at ν = 2168 cm⁻¹ that becomes stronger as the potential increases, which can be attributed to CNO⁻ intermediate.[22] As be clearly seen, the vibration peak of CNO⁻ intermediate becomes much more pronounced for NiClO-D catalyst than that of NiOH-D catalyst as the measurement time increases. Such an observation reflects that the NiClO-D catalyst has faster reaction kinetics than NiOH-D catalyst. Besides, strong C=O vibration peaks at ν = 1720 cm⁻¹ are observed in the spectra of the NiOH-D catalyst,[23] while no obvious accumulations of C=O intermediates are found for the NiClO-D catalyst. In the lattice-oxygen-involved reaction pathway for NiClO-D catalyst discussed above, C=O intermediate is more facilely converted to COO⁺ intermediate and then CO₂ gas. Notably, the spectra of NiClO-D catalyst (Figure 4c) indeed feature CO₂ vibration peaks located at ν = 2390 cm⁻¹ while no sign of CO₂ vibration peaks is found for NiOH-D catalyst.[24] Since the generated CO₂ gas is easy to react with KOH aqueous electrolyte, these results indicate much more amount of CO₂ gas generated from NiClO-D under the same experimental condition, suggesting the faster reaction kinetics of NiClO-D catalyst compared with NiOH-D catalyst.

Note that the spectra of NiOH-D catalyst (Figure 4d) feature a vibration peak at ν = 1635 cm⁻¹, which is assigned to N–H vibration in amide (–CONH₂) groups.[25] In contrast, no sign of such vibration peak is found in the spectra of NiClO-D catalyst. As shown by DFT simulation, the step of forming -CONH₂ group in the conventional pathway is replaced by the lattice-oxygen-involved COO⁺ formation step in the new pathway. These results provide spectroscopic evidence for the two different reaction pathways for NiClO-D and NiOH-D catalysts. The faster kinetics for CNO⁻ formation and adsorbed +COO⁻ desorption of NiClO-D catalyst correlate well with its enhanced catalytic performance. Moreover, the lower energy barrier of +COO⁻ desorption can greatly diminish the deactivation of active sites, enabling the high stability of NiClO-D catalyst.
In summary, we demonstrate a novel and efficient lattice-oxygen-involved reaction pathway on Ni\textsuperscript{4+} active sites for electrocatalytic urea oxidation, as verified by electrochemical results, isotope-labeling mass spectrometry, and in situ infrared spectroscopy. The increased oxidation state of metal sites not only governs the UOR activity but also the reaction mechanism, where lattice oxygen can be activated for UOR and promote new reaction pathways. This work provides insights for further advances to the development of electrocatalysts via oxidation state modulation.

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Conflict of interest

The authors declare no conflict of interest.

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