Two-dimensional nickel hydroxide nanosheets with high-content of nickel (III) species towards superior urea electro-oxidation

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\textbf{ABSTRACT}

Development of high-efficient and stable electrocatalysts for urea oxidation reaction (UOR) is of a great challenge due to the sluggish kinetics of 6\textsuperscript{e}\textsuperscript{−} electron transfer process. Here, we have developed a facile and easy-to-scale approach to fabricate two-dimensional Ni(III)-rich Ni(OH)\textsubscript{2} nanosheets on amine-functionalized carbon (Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2}). Morphological characterizations confirm the existence of nanosheets, and XPS spectra indicate that the content of Ni\textsuperscript{3+} species in Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} (ca. 57.6\%) is significantly higher than that of in Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} (ca. 43.1\%) and Ni(OH)\textsubscript{2}/C (ca. 20.7\%). Electrochemical analyses illustrate that the as-prepared Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst exhibits the highest current density (91.72 mA cm\textsuperscript{−}2) at a potential of 0.61 V, which is 2.06-, 2.08- and 3.47-fold higher than that of Ni(OH)\textsubscript{2}/C-NH\textsubscript{2}, Ni(OH)\textsubscript{2}/C and Pt/C, respectively. Moreover, the Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst also demonstrates an outstanding voltammetric cycles and long-term chronoamperometric stability. The superior electrocatalytic activity and stability could be ascribed to the synergistic effect of Ni\textsuperscript{3+} doping as well as the amine-functionalized carbon, where higher concentration Ni\textsuperscript{3+} species in Ni(OH)\textsubscript{2} sheets could provide more active sites for adsorption and transformation of urea molecules, while fluffy C-NH\textsubscript{2} support could enhance the ability of solute diffusion, electron transport and gas emissions, thereby dramatically improve the catalytic activity.

1. Introduction

The demands for sustainable green energy and zero-tolerance on environmental pollution have emerged as typical themes of social and economic development [1,2]. The recent studies show that 2–2.5\% urea contaminated wastewaters were released from various industrial streams [3]. The presence of urea in wastewater streams is a serious problem since it is eventually hydrolyzed into ammonia, which results increasing pH of the soil as well as contributing to the greenhouse effect when it is released to the atmosphere [4]. Consequently, it is of great significance to eliminate the environmental pollution of urea from the source. A wide range of processes has been investigated in this regards including electrochemical oxidation, physical adsorption, and biological decomposition [5–7]. Most of these approaches require complicated equipment and a high-energy input thereof limited at industrial application. Direct urea fuel cells (DUFC) has been shown to be a promising approach since it converts urea into N\textsubscript{2} and CO\textsubscript{2} while generating electricity [8]. However, the challenge lays on how to overcome the sluggish kinetics of 6\textsuperscript{e}\textsuperscript{−} electron transfer [9]. The elemental doping approaches were proven to be one of the effective strategies deal with this kind of problems in the fields of water splitting [10–12], fuel cells [13–15], photocatalysis [16–18], gas capture [19,20], and so on. In general, doping a hetero-element inevitably increases the structural defects, which in turn leads to the degradation of the catalytic performance [21,22]. Conversely, homo-species doping, where the same element with different chemical states is incorporated into the crystal lattice, considered to be a very promising strategy for enhancing catalytic performance because it does not cause significant structural distortion thereof less defects compared to the heterogeneous doping [17]. Although there are two types of catalysts based on Ni and Mn elements which are being used for urea oxidation, Ni-based catalyst is more preferred over Mn-based catalysts because Mn-based catalyst requires higher overpotential and shows less efficiency [23,24] compare to that of Ni-based catalysts [25–27]. It is a well acknowledged fact that Ni(OH)\textsubscript{2} to NiOOH is the critical step before electrocatalytic urea oxidation (Ni(OH)\textsubscript{2} + OH\textsuperscript{−} → NiOOH + H\textsubscript{2}O + e\textsuperscript{−}) [27]. Furthermore,
calculations also show that urea molecules are more easily adsorbed onto the surface of NiOOH species [28]. In other words, increasing NiOOH content in the catalyst should significantly improve the catalytic performance of urea oxidation. To the best of our knowledge, there are rarely reports in this regard, including exfoliated nickel hydroxide nanosheets [29], S-doped Ni(OH)2 [9], α-Ni(OH)2@CNT [30], etc. Therefore, exploring the effect of NiOOH species in homogeneous catalyst for urea electro-oxidation is still of great significance.

Herein, we report a facile method of doping of Ni$^{3+}$ species in 2D Ni(OH)2 sheets by ammonia evaporation assisted method in the presence of Ni(NO3)2, and XC-72 carbon. The as-prepared Ni$^{3+}$-rich Ni(OH)2/C-NH2 catalyst exhibits the highest catalytic activity towards urea electro-oxidation in alkaline solution, which is 2.06-, 2.08- and 3.47-fold higher than Ni(OH)2/C-NH2, Ni(OH)2/C and Pt/C, respectively. Moreover, the Ni$^{3+}$-rich Ni(OH)2/C-NH2 catalyst also exhibits an outstanding stability in 1.0 M KOH + 0.33 M urea solution for continuous running of 2.0 h. The superior catalytic activity and stability could be ascribed to the presence of NiOOH spaces through Ni$^{3+}$ doping in the β phase of 2D Ni(OH)2 sheets as well as the synergistic effect between Ni(OH)2 and amine-fuctionalized carbon support. The catalytic mechanism of the hybrid catalyst for urea electro-oxidation has also been proposed and discussed in detail in this work.

2. Experimental

2.1. Synthesis of Ni$^{3+}$-rich Ni(OH)2/C-NH2

All chemical reagents are analytical grade and used without further purification. 313.6 mg Ni(NO3)2·6H2O and 100 mg XC-72 carbon were dispersed into a mixture solution (40 mL NH3·H2O + 30 mL H2O + 10 mL ethanol) in a glass beaker. After sonication for 30 min and subsequently stirred for 4 h. The resultant mixture solution was heated at 120 °C to evaporate the solvent without stirring for several hours. The residual product was collected, washed three times with H2O-ethanol mixture and then freeze dried at −37 °C for 12 h. The resulting products were labeled as Ni$^{3+}$-rich Ni(OH)2/C-NH2. For better comparison, the Ni(OH)2/C-NH2 was prepared under the same condition as above without the simultaneous heating and no stirring.

The Ni(OH)2/C was prepared as follows, 313.6 mg Ni(NO3)2·6H2O and 100 mg XC-72 carbon were added into a mixture solution of 15 mL H2O and 5 mL ethanol. After sonicated for 30 min, 20 mL of 0.107 M NaOH solution was dropped slowly under vigorously stirring. Four hours later, the products were centrifuged, washed with a water-ethanol mixture, and then freeze dried. The pure Ni(OH)2 was purchased from Macklin biochemical company.

2.2. Catalyst characterizations

X-ray diffraction (XRD) pattern was initially used to track the crystal structures of as-prepared Ni$^{3+}$-rich Ni(OH)2/C-NH2, Ni(OH)2/C-NH2 and Ni(OH)2/C materials. As shown in Fig. 1a, we can see that the three samples show similar peaks in the range of 10° to 90°, which are consistent with the typical diffraction peaks of Ni(OH)2 (JCPDS: 14-0117) [31]. It is noteworthy that the diffraction peaks of Ni$^{3+}$-rich Ni(OH)2/C-NH2 are much higher and stronger than that of others, indicating better crystallinity. Moreover, there are two additional peaks at ~ 25.0° and 44.4° can be attributed to the hexagonal phase of carbon (002) and (101), respectively [32]. Specially, there is a typical peak at 12.7° in 2D Ni$^{3+}$-rich Ni(OH)2/C-NH2 spectrum, which is corresponding to the crystal facet (003) of NiOOH (JCPDS: 06-0075), indicating that the Ni$^{3+}$ species are well-doped in Ni(OH)2 structures.

The morphology of the synthesized materials is identified by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1b, we can see that the sheet-like structural Ni$^{3+}$-rich Ni(OH)2 and amine functionalized carbon support are randomly distributed in the whole range, and the Ni$^{3+}$-rich Ni(OH)2 sheets exhibit two-dimensional structures with thickness of ca. 27 ± 3 nm and width of ca. 1.0 ± 0.2 µm. TEM image mapping indicates that the elements of Ni, N, C and O are uniformly distributed throughout the catalyst (Fig. S1). However, if the material is synthesized at similar experimental conditions with continuous stirring at 120 °C (named as Ni(OH)2/C-NH2), we can see that the needle-like Ni(OH)2 species are uniformly distributed on the surface of amine functionalized carbon support (Fig. S2a). Correspondingly, if the material is prepared by NaOH precipitation under continuous stirring, the Ni(OH)2 particles are well distributed together with the carbon support (Fig. S2b). TEM and high-resolution TEM images are used to further explore the microstructures of Ni$^{3+}$-rich Ni(OH)2/C-NH2 material. As shown in Fig. 1c, the sheet-like Ni$^{3+}$-rich Ni(OH)2 material is interwovenly distributed on the amine functionalized carbon substrate to form a uniform hybrid system. The high-resolution TEM image displays clear lattice fringes with spacings ca. 0.23 and 0.27 nm (Fig. 1d), corresponding to the (101) and (100) crystal facets of Ni(OH)2, respectively. More importantly, many previous works confirmed that two-dimensional materials could expose more low-coordinated steps surface than other structures [33,34], thereby they can provide abundant active sites to adsorb reactant molecules, accelerate the reaction speed and mediate the catalytic activity.

2.3. Electrochemical measurements

Biologic VMP3 electrochemical workstation was operated to measure all the electrochemical data, in which saturated calomel electrode (SCE), Pt sheet (1 cm × 2 cm) and glassy carbon electrode (GCE, ϕ = 3 mm) were used as the reference, counter and working electrodes, respectively. The GCE was polished to a mirror-like surface by α-Al2O3 powder with different sizes. The surface was thoroughly washed with copious acetone, ethanol, and H2O. 2.0 mg samples were dissolved in a mixture solution (400 µL) of H2O and ethanol with a volume ratio of 1:1. After ultrasonicated for 30 min, 28 µL of the suspension was dropped onto the polished GCE surface. Then, 5 µL of 0.5% Nafion solution was pipetted to fix the catalyst on the electrode surface. The loading of Ni(OH)2 was kept at ca. 1.0 mg cm−2 for all the catalysts.

The electrochemical performances of all the catalysts were evaluated in N2-saturated 1.0 M KOH and 1.0 M KOH + 0.33 M urea solution. Cyclic voltammetry (CV) was conducted in the range of 0 to 0.5 V in N2-saturated 1.0 M KOH solution and operated in the range of 0 to 0.8 V in N2-saturated 1.0 M KOH + 0.33 M urea solution. The long-term stability of different catalysts was tested at a fixed potential in N2-saturated 1.0 M KOH + 0.33 M urea for 7200 s. All the electrochemical results are respect to the SCE reference and all the experiments were carried out at room temperature (25 ± 0.5 °C).

3. Results and discussion

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855.3 and 856.5 eV are corresponding to Ni(OH)$_2$ and NiOOH, respectively [35]. We can see that the contents of NiOOH species in the hybrid catalysts are in the order of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ (ca. 57.6%) > Ni(OH)$_2$/C-NH$_2$ (ca. 43.1%) > Ni(OH)$_2$/C (ca. 20.7%), indicating that the Ni$^{3+}$ species are much easier to be formed under steady-state conditions in ammonia solution at 120 °C. Furthermore, the

![Graph showing XRD patterns of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$, Ni(OH)$_2$/C-NH$_2$, and Ni(OH)$_2$/C.](image)

Fig. 1. (a) XRD patterns of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$, Ni(OH)$_2$/C-NH$_2$, and Ni(OH)$_2$/C. (b) SEM image of the synthesized Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$. (c) TEM and (d) high-resolution TEM images of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$.

![SEM image and high-resolution TEM images of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$.](image)

Fig. 2. (a) High-resolution Ni 2p$_{3/2}$ XPS spectrum of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$, Ni(OH)$_2$/C-NH$_2$, and Ni(OH)$_2$/C. (b) High-resolution N 1s XPS spectrum of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$. (c) Thermogravimetric (TG) analysis of Ni$^{3+}$-rich Ni(OH)$_2$ and Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ in O$_2$ atmosphere with a rising temperature rate of 2.5 °C min$^{-1}$.
As shown in Fig. S3, the elements of C, N, O, and Ni exist in Ni\textsuperscript{3+}-rich (399.1 eV) and residual nitrate (406.3 eV), respectively (Fig. 2b) [36].

A high-resolution N 1 s spectrum is also detected and assigned to amino-N. Consecutive cyclic voltammograms (CVs) of (a) Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} and (b) Ni(OH)\textsubscript{2}/C catalysts in N\textsubscript{2}-saturated 1.0 M KOH solution with a scan rate of 30 mV s\textsuperscript{-1}. (c) The extracted second cycles from CVs of the synthesized three samples. (d) CVs of Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst in N\textsubscript{2}-saturated 1.0 M KOH with different scan rates in the range of 10 to 100 mV s\textsuperscript{-1}. (e) Peak current densities versus the scan rates (10–40 mV s\textsuperscript{-1}) of Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst. (f) The peak current densities versus square roots of synthesized different catalysts in the range of 50 to 100 mV s\textsuperscript{-1}.

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High-resolution N 1 s spectrum is also detected and assigned to amino-N in alkaline solution [40]. In contrary, the current densities of Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst due to the interconversion of Ni(OH)\textsubscript{2} and α-Ni(OH)\textsubscript{2} phases have coexisted under steady-state conditions [41]. The coexistence of γ-NiOOH with α-Ni(OH)\textsubscript{2} species is associated with swelling or volume expansion of the catalyst, therefore, causes microcracks and disintegrates, and subsequently increases the internal resistance and reduces the catalyst efficiency [42].

The electrochemically active surface area (ESA) of the three samples are further investigated through the cathodic reduction peaks of NiOOH/C-NH\textsubscript{2} on the catalyst surface from the backward scan [28, 43]. The peak intensity is proportional to the number of active sites exposed for urea electro-oxidation. The ESA of different catalysts are calculated using the equation of ESA = Q / mg, where Q is the amount of total charge requested to reduce NiOOH to Ni(OH)\textsubscript{2} and m is the amount of Ni in the hybrid catalysts, and q is 257 μC cm\textsuperscript{-2}. As shown in Fig. S5, the ESA values are 88.6, 83.6 and 217.2 m\textsuperscript{2} g\textsuperscript{-1} for Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2}, Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} and Ni(OH)\textsubscript{2}/C respectively, indicating the crucial role of β-NiOOH phase on urea electrooxidation.

Electrochemical studies are performed in order to evaluate the transformation of constituent species in the hybrid catalysts in 1.0 M KOH solution. Each solution was purged with high-purity N\textsubscript{2} gas for 15 min at room temperature before the measurements. As shown in Fig. 3a, the consecutive CV curves of Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst are recorded in the range of 0 to 0.5 V with a scan rate of 30 mV s\textsuperscript{-1} for different cycles. A pair of redox peaks were observed on Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst due to the interconversion of Ni(OH)\textsubscript{2} and NiOOH (Ni(OH)\textsubscript{2} + OH\textsuperscript{−} ↔ NiOOH + H\textsubscript{2}O + e\textsuperscript{−}) [38,39]. In the consecutive CVs, the peak intensity increases gradually with the increase of the number of cycles, while the current enhancements are considered to be the progressive enrichment of the accessible electroactive species (Ni\textsuperscript{3+} and Ni\textsuperscript{2+}) on or near the surface [40]. In addition, the peak potentials are almost same, suggesting no phase transformation of NiOOH from β to γ occurred during the measurements. Meaning, a high catalytic performance can be expected from this material since the β-NiOOH phase is proven to have a superior electrochemical performance in alkaline solution [40].

In contrary, the current densities of Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} declined gradually with increasing number of CV cycles owing to the agglomerations during the reaction (Fig. S5). The Ni(OH)\textsubscript{2}/C catalyst shows an apparently negative shifts both at anodic and cathodic peak potentials with increasing number of CV cycles (Fig. 3b), which was resulted from the physical transformations of Ni(OH)\textsubscript{2} species when the γ-NiOOH and α-Ni(OH)\textsubscript{2} phases have coexisted under steady-state conditions [41]. The coexistence of γ-NiOOH with α-Ni(OH)\textsubscript{2} species is associated with swelling or volume expansion of the catalyst, therefore, causes microcracks and disintegrates, and subsequently increases the internal resistance and reduces the catalyst efficiency [42].

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NH$_2$ catalyst exhibits an onset potential at ca. 0.33 V, which is slightly lower than that of Ni(OH)$_2$/C-NH$_2$ at ca. 0.31 V, meanwhile notably higher than those of Ni(OH)$_2$/C-NH$_2$ at ca. 0.36 V, Ni$^{3+}$-rich Ni(OH)$_2$ at ca. 0.37 V and Pt/C at ca. 0.34 V. After that, the current densities increase gradually with increase of the applied potentials until reach the peak potentials. As a result, the Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ catalyst shows the highest current density (91.71 mA cm$^{-2}$) during the forward scan in urea electro-oxidation. The resulting current density is 2.06-, 2.08-, 2.89- and 2.47-fold higher than that of Ni(OH)$_2$/C-NH$_2$ (44.53 mA cm$^{-2}$), Ni(OH)$_2$/C (44.01 mA cm$^{-2}$), Pt/C (26.41 mA cm$^{-2}$) and Ni$^{3+}$-rich Ni(OH)$_2$ (31.76 mA cm$^{-2}$), respectively. The greatly improved current density of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ catalyst can be ascribed to the stable 2D structures exposing more active sites and more β-NiOOH species on the surface rather than γ-NiOOH species. Besides, the fluffy C-NH$_2$ support also plays an important role in improving the catalytic activity due to the increasing of solute diffusion, electron transport, and final gas emissions. A slight degradation of catalytic activity after peak potentials and lower reverse current densities can be caused by the gas bubbles of the final products (e.g., CO$_2$, N$_2$) blocking the active sites during the reaction, which subsequently inhibit the adsorption of urea molecules from the electrolyte. Fig. 4b shows the continuous CV curves for 100 cycles in 1.0 M KOH + 0.33 M urea solution with a scan rate of 50 mV s$^{-1}$. Repeated CVs of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ catalyst in 1.0 M KOH + 0.33 M urea solution under (b) static testing condition and (c) rotating disk electrode with 1600 rpm at a scan rate of 50 mV s$^{-1}$. (D) Chronoamperometric curves of different catalysts at a fixed potential of 0.35 V in 1.0 M KOH + 0.33 M urea solution.

In order to evaluate the long-term stability of these catalysts for urea oxidation, the chronoamperometric measurements are performed at a constant potential (0.35 V) in 1.0 M KOH + 0.33 M urea solution at 25°C for 120 min. Although the current densities of all the catalysts decrease rapidly at the initial stage as shown in Fig. 4d, the Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ catalyst shows the highest initial and final current densities in the whole process. This catalyst demonstrates promising activities for UOR application [9].

3.4. Catalytic mechanism

The entire catalytic process of Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ catalyst for urea electro-oxidation could be explained as following three steps (Fig. 5a–b). (1) Adsorption of urea molecules and OH$^-$ ions to the active sites of Ni$^{3+}$-doped Ni(OH)$_2$ sheets. (2) Gradual oxidation of Ni(OH)$_2$ species on the catalyst surface into NiOOH species (Ni(OH)$_2$ + OH$^-$ ↔ NiOOH + H$_2$O + e$^-$) [45]. (3) The urea oxidation by NiOOH to N$_2$ and CO$_2$ molecules while itself becoming Ni(OH)$_2$ to complete the catalytic cycle. As discussed above, the two-dimensional Ni$^{3+}$-rich Ni(OH)$_2$ sheets reported here is mainly transformed into β-NiOOH species rather than γ-NiOOH species and yet the Ni$^{3+}$-rich Ni(OH)$_2$/C-NH$_2$ catalyst shows the highest catalytic activity for urea electro-oxidation among all the other catalysts. Therefore, it can be concluded that β-NiOOH species have higher catalytic activity for urea electro-oxidation in alkaline solution than γ-NiOOH species. Furthermore, the amine groups on the carbon support not only improved surface attachment of Ni(OH)$_2$ but also attracting the reactant through hydrogen bonding. In addition, it also facilitated the directional conversion of β-Ni(OH)$_2$ species to β-NiOOH species. Finally, we believe that the high concentration of β-
NiOOH species and the synergy between catalyst and support are the two main reasons for the better catalytic performance.

4. Conclusion

In summary, we have developed a facile approach to fabricate 2D Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2} sheets on amine functionalized carbon. The as-prepared catalyst exhibits an enhanced electrocatalytic activity and excellent durability for urea electro-oxidation in alkaline solution compared to Ni(OH)\textsubscript{2}/C-NH\textsubscript{2}, Ni(OH)\textsubscript{2}/C, Pt/C and Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2} catalysts. This superior electrocatalytic performance towards the urea electro-oxidation could be ascribed to the higher concentration of β-NiOOH intermediated and the synergistic effect of Ni\textsuperscript{3+} species doping, 2D structural Ni(OH)\textsubscript{2} sheets and amine functionalized carbon in the hybrid catalyst. Besides, considering the low cost of carbon and Ni salt, the 2D structural Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst may have practical applications in DUFC and other areas (e.g., lithium battery, water splitting, etc.).

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Notes

The authors declare no competing financial interest.

Appendix A. Supplementary data

Figs. S1–S6 and Tables S1 give more details on characterization of our synthesized materials and their electrocatalytic performance data; additional SEM, XPS, TG, and electrocatalytic performance data (PDF).

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2018.10.007.

References


Fig. 5. (a) Schematic description of the transformation of Ni(OH)\textsubscript{2} and NiOOH species and their electro-oxidation of urea on the surface of Ni\textsuperscript{3+}-rich Ni(OH)\textsubscript{2}/C-NH\textsubscript{2} catalyst in alkaline solution. (b) Catalytic mechanism diagram of the formed NiOOH species on the hybrid catalyst surface for electrocatalytic oxidation of urea molecules in alkaline solution.