Operando Converting BiOCl into Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ for Efficient Electrocatalytic Reduction of Carbon Dioxide to Formate

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HIGHLIGHTS

- An operando synthetic approach was exemplified to enhance catalyst stability for efficient reduction of CO$_2$ to formate.
- A highly stable Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ electrocatalyst was synthesized by direct electrochemical conversion of BiOCl via a cathodic potential-promoted anion-exchange process under operando CO$_2$RR conditions.
- The surface Cl$^-$ in Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ changes the p-orbital electron states to enhance the stability and alters the CO$_2$RR pathway to markedly reduce the energy barrier.

ABSTRACT Bismuth-based materials (e.g., metallic, oxides and subcarbonate) are emerged as promising electrocatalysts for converting CO$_2$ to formate. However, Bi$^3+$-based electrocatalysts possess high overpotentials, while bismuth oxides and subcarbonate encounter stability issues. This work is designated to exemplify that the operando synthesis can be an effective means to enhance the stability of electrocatalysts under operando CO$_2$RR conditions. A synthetic approach is developed to electrochemically convert BiOCl into Cl-containing subcarbonate (Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$) under operando CO$_2$RR conditions. The systematic operando spectroscopic studies depict that BiOCl is converted to Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ via a cathodic potential-promoted anion-exchange process. The operando synthesized Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ can tolerate −1.0 V versus RHE, while for the wet-chemistry synthesized pure Bi$_2$O$_2$CO$_3$, the formation of metallic Bi$^0$ occurs at −0.6 V versus RHE. At −0.8 V versus RHE, Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ can readily attain a FE$_{\text{HCOO}^-}$ of 97.9%, much higher than that of the pure Bi$_2$O$_2$CO$_3$ (81.3%). DFT calculations indicate that differing from the pure Bi$_2$O$_2$CO$_3$-catalyzed CO$_2$RR, where formate is formed via a "OCHO intermediate step that requires a high energy input energy of 2.69 eV to proceed, the formation of HCOO$^-$ over Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ has proceeded via a "COOH intermediate step that only requires low energy input of 2.56 eV.

KEYWORDS Carbon dioxide reduction; Chloride-containing bismuth subcarbonate; Cathodic potential-promoted anion-exchange; Stability
1 Introduction

The renewable electricity-powered electrocatalytic carbon dioxide reduction reaction (CO$_2$RR) to produce chemicals/fuels not only curbs greenhouse gas emissions but also reduces our reliance on the rapidly diminished petroleum resources [1]. In this regard, various C$_1$ (e.g., carbon monoxide, formate, methane and methanol), C$_2$ and C$_2$+ (e.g., ethylene, ethanol, acetylene, acetate, acetaldehyde, oxalic acid and n-propanol) CO$_2$RR products have been obtained [2, 3]. Among them, CO and HCOO$^-$/HCOOH are the most energy-efficient CO$_2$RR products as they can be formed by transferring two electrons to CO$_2$. Comparing to CO, converting CO$_2$ to HCOO$^-$/HCOOH is more desirable because HCOO$^-$/HCOOH are more valuable commodity chemicals [4, 5]. To date, the reported high-performance electrocatalysts for CO$_2$ reduction to HCOO$^-$/HCOOH are almost exclusively made of p-block metals-based materials such as In, Pb, Sn, Sb and Bi [6, 7].

Owing to their low toxicity and high selectivity toward HCOO$^-$/HCOOH, Bi-based CO$_2$RR electrocatalysts have attracted increasing attentions [8, 9]. Various Bi-based CO$_2$RR electrocatalysts such as metallic Bi$^o$, oxides and subcarbonate (Table S1) have been employed to electrocatalytically convert CO$_2$ to HCOO$^-$/HCOOH. As shown in Table S1, in general, the metallic Bi$^o$-based ones perform better than other forms of bismuth-containing electrocatalysts. Nevertheless, the metallic Bi$^o$-based electrocatalysts usually require high overpotentials, consequently the high cathodic potentials, to achieve their optimal performances [10, 11], undesirable for energy efficiency. In addition, high cathodic potentials are favorable for the competing hydrogen evolution reaction (HER), which often leads to low Faradic efficiencies toward HCOO$^-$/HCOOH (FE$_{\text{HCOO}^-}$/FE$_{\text{HCOOH}}$) [12]. The bismuth oxides-based electrocatalysts were also reported (Table S1). Noticeably, such electrocatalysts often encounter stability issues because the bismuth oxides in these electrocatalysts can be easily converted to metallic Bi$^o$ under CO$_2$RR conditions [13]. For example, Deng et al. reported a Bi$_2$O$_3$ electrocatalyst with the optimal performance at $-0.9$ V (vs RHE) to achieve a FE$_{\text{HCOO}^-}$ of $91\%$ with a partial HCOO$^-$ current density ($i_{\text{HCOO}^-}$) of $\approx 8$ mA cm$^{-2}$ [14]. However, the as-synthesized Bi$_2$O$_3$ is found to be partially converted to metallic Bi$^o$ under the CO$_2$RR conditions at $-0.9$ V vs RHE. In fact, the reported bismuth oxides electrocatalysts require cathodic potentials $\geq -0.9$ (vs RHE) to concurrently achieve FE$_{\text{HCOO}^-}$ $> 90\%$ with $J_{\text{HCOO}^-} \geq 15$ mA cm$^{-2}$ [13, 15, 16]. Under such CO$_2$RR conditions, the bismuth oxides in these electrocatalysts are either partially or completely converted to metallic Bi$^o$. Other than metallic Bi$^o$ and bismuth oxides, Zhang’s group reported the use of ultrathin bismuth subcarbonate (Bi$_2$O$_2$CO$_3$) nanosheets to catalyze CO$_2$ reduction to HCOO$^-$ [17]. Their Bi$_2$O$_2$CO$_3$ electrocatalyst exhibits a very low overpotential of 610 mV and can achieve a FE$_{\text{HCOO}^-}$ of 85% with a $J_{\text{HCOO}^-}$ of $\approx 11$ mA cm$^{-2}$ at $-0.7$ V (vs HRE), however, partial conversion of Bi$_2$O$_2$CO$_3$ to the metallic Bi$^o$ occurs within 30 min under $-0.65$ V (vs RHE).

As reviewed above, under the required cathodic potentials to concurrently achieve high FE$_{\text{HCOO}^-}$ and $J_{\text{HCOO}^-}$, the reported bismuth oxide and subcarbonate electrocatalysts are unavoidably reduced to metallic Bi$^o$, leading to the structural and compositional changes under operando CO$_2$RR conditions. Critically, such operando structural transformation processes are progressive and potential-dependent, leading to great difficulties to confirm the actual active sites, hence the catalysis mechanisms. Parenthetically, the synthetic conditions of the reported bismuth oxide and subcarbonate electrocatalysts are vastly different to their electrocatalytic application conditions, which could be a cause of their structural transformation under the operando CO$_2$RR conditions. If this is true, the severe operando stability issues might be effectively mitigated by employing identical synthesis and application conditions.

In this contribution, we report an approach to electrochemically convert bismuth oxychloride (BiOCl) into chloride-containing bismuth subcarbonate (Bi$_2$O$_2$(CO$_3$)$_2$Cl) under operando CO$_2$RR conditions (at $-0.8$ V vs RHE in CO$_2$-saturated 0.5 M KHCO$_3$ solution) and use it to exemplify that the operando synthesis can be an effective means to enhance the operando electrochemical stability of electrocatalysts. Systematic operando spectroscopic studies were conducted to depict the conversion mechanism and electrochemical stability. BiOCl is converted to Bi$_2$O$_2$(CO$_3$)$_2$Cl$_x$ via the cathodic potential-promoted anion-exchange process. The obtained Bi$_2$O$_2$(CO$_3$)$_2$Cl$_x$ can tolerate $-1.0$ V versus RHE, while for the wet-chemistry synthesized pure tetragonal phased Bi$_2$O$_2$CO$_3$, the formation of metallic Bi$^o$ occurs at $-0.6$ V versus RHE, signifying a markedly improved electrochemical
stability. No notable structural change and performance decay are observed when Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ is subjected to the stability test at −0.8 V versus RHE over a 20 h period. At −0.8 V versus RHE, Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ can readily attain a $\text{FE}_{\text{HCOO}^-}$ of 97.9%, much higher than that of Bi$_2$O$_2$CO$_3$ (81.3%). The density functional theory (DFT) calculations indicate that differing from Bi$_2$O$_2$CO$_3$-catalyzed CO$_2$RR, where HCOOH is formed via a $^*$OCHO intermediate step that requires a high energy input energy of 2.69 eV to proceed, the formation of HCOOH over Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ has proceeded via a $^*$COOH intermediate step that requires a notably reduced energy input of 2.56 eV.

2 Experimental and Calculation

2.1 Materials and Chemicals

Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, 99%), potassium chloride (KCl, 99.5%), ethanol (C$_2$H$_5$OH, 99%) and ethylene glycol (C$_2$H$_6$O$_2$, 99.8%) were purchased from Chem-Supply. Urea (CH$_4$N$_2$O), Nafion (5 wt%) was purchased from Sigma-Aldrich. Carbon paper (TGP-H-060) and Nafion 115 proton exchange membrane were purchased from Alfa Aesar. The carbon paper was ultrasonically treated in deionized water and ethanol, followed by emerging in the concentrated HNO$_3$ at 100 °C for 12 h, thoroughly washed with the deionized water and ethanol and dried in air.

2.2 Synthesis of BiOCl-NSs

0.164 g of KCl and 0.868 g of Bi(NO$_3$)$_3$·5H$_2$O were dissolved in 70 mL H$_2$O and stirred for 1 h. The solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 120 °C for 24 h. The obtained BiOCl-NSs was adequately washed with deionized water and ethanol and dried at 60 °C for 6 h in vacuum oven.

2.3 Synthesis of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$

Twenty milligrams of the as-synthesized BiOCl-NSs was mixed with 80 μL Nafion solution (5 wt%) and dispersed 0.92 mL isopropanol under sonication for 40 min to form the ink. 100 μL ink was then cast onto the pre-treated carbon fiber paper substrate with an exposed area of 1 × 1 cm$^2$ (2 mg cm$^{-2}$ of BiOCl-NSs). The carbon fiber paper with loaded BiOCl-NSs was used as the working electrode and subjected to −0.8 V (vs RHE) in CO$_2$-saturated 0.5 M KHCO$_3$ solution for 2 h to electrochemically transform BiOCl-NSs to Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$.

2.4 Synthesis of Bi$_2$O$_2$CO$_3$

For comparative purpose, pure Bi$_2$O$_2$CO$_3$ was synthesized. Under constant stirring, 0.234 g of Bi(NO$_3$)$_3$·5H$_2$O was dissolved into 10 mL H$_2$O, followed by adding 1.502 g of CH$_4$N$_2$O and 10 mL of C$_2$H$_5$OH. The resultant solution was then placed in the oil bath under 90 °C for 4 h. The obtained pure Bi$_2$O$_2$CO$_3$ was adequately washed with deionized water and ethanol and dried in a vacuum oven of 60 °C for 6 h.

2.5 Electrochemical Measurements

The electrochemical measurements were performed using a Nafion 115 proton exchange membrane separated two-compartment electrochemical cell consisting of a three-electrode system controlled by an electrochemical station (CHI 660E). For CO$_2$RR, the Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ working electrode (1 × 1 cm$^2$) was fabricated by operando electrochemical transformation of the immobilized BiOCl-NSs on carbon fiber paper, while the Bi$_2$O$_2$CO$_3$ working electrode was prepared by immobilizing 2 mg cm$^{-2}$ of Bi$_2$O$_2$CO$_3$ on carbon fiber paper (1 × 1 cm$^2$). For all electrochemical measurements, an Ag/AgCl (3.5 M KCl) reference electrode, a Pt mesh counter electrode and CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte (pH of 7.2) were employed. During CO$_2$RR, the electrolyte in the cathode compartment was constantly stirred at a rate of 800 rpm and bubbled with CO$_2$ at a flow rate of 5 mL min$^{-1}$ controlled by a universal flow meter (Alicat Scientific, LK2). All reported potentials were converted to the reversible hydrogen electrode (RHE) in accordance with $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.205$. The gas chromatography (GC, RAMIN, GC2060) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used to qualitatively and quantitatively determine the gaseous products (e.g., H$_2$ and CO or other gaseous hydrocarbons). The CO and H$_2$ Faradaic efficiency were calculated as below:

$$\text{FE}_{\text{CO}} = 2\times\text{CO}\%\text{GF}/\text{IRT}$$ (1)
\[ \text{FE}_{\text{H}_2} = 2x_{\text{H}_2}pGF/IRT \]  
(2)

where \( x_{\text{CO}} \) and \( x_{\text{H}_2} \) (vol\%) are the volume fractions of CO and H\(_2\) in the exhaust gas, \( I \) (A) is the steady-state current, \( G = 5 \text{ mL min}^{-1} \) is the CO\(_2\) flow rate, \( \rho = 1.013 \times 10^5 \text{ Pa}, \) \( T = 273.15 \text{ K}, F = 96,485 \text{ C mol}^{-1}, R = 8.3145 \text{ J mol}^{-1 \text{ K}^{-1}}. \)

\(^1\text{H}\) nuclear magnetic resonance \((^{1}\text{H-NMR})\) was used to qualitatively and quantitatively determine the liquid phase products, including HCOOH. After reaction, 0.5 mL electrolyte from the cathode compartment was mixed with 0.1 mL D\(_2\)O containing 3-(trimethylsilyl)propanoic acid (TMSP) as the internal standard and subjected to NMR analysis. The Faradaic efficiency for formation of HCOO\(^-\) was calculated as below:

\[ \text{FE} = 2F \times n_{\text{HCOO}^-}/(I \times t). \]  
(3)

### 2.6 Characterizations

The morphologies and structures of the samples were characterized by SEM (JEOL JSM-7100) and TEM (Tecnai F20, 200 kV). The STEM images were recorded using a probe corrected JEOL JEM-ARM200F instrument with an acceleration voltage of 200 kV. AFM measurements were performed using a Bruker Dimension Icon system. XRD patterns were collected from a Bruker D8 diffractometer. The \textit{operando} XRD patterns were recorded using a Bruker D8 diffractometer and a home-made three-electrode electrochemical cell. The \textit{operando} Raman studies were performed on a RENISHAW mVia Raman Microscope equipped with a microscopic lens immersed under the electrolyte to capture Raman signals and a home-made three-electrode electrochemical cell consisting of a BiOCl-NSs or Bi\(_2\)O\(_2\)CO\(_3\) working electrode, an Ag/AgCl (3.5 M KCl) reference electrode and a Pt mesh counter electrode. The working electrodes were prepared by immobilizing BiOCl-NSs or Bi\(_2\)O\(_2\)CO\(_3\) on a commercial Si substrate \((1 \times 1 \text{ cm}^2)\). XPS spectra were recorded by Kratos Axis ULTRA using the C\(_1\)s at 284.8 eV as the internal standard. C and O K-edge XAS measurements were performed at the Soft X-ray spectroscopy beamline at Australian Synchrotron Facility, Australia’s Nuclear Science and Technology Organisation (Clayton, Victoria, Australia). Bi L\(_{3}\)-edge XAS measurements were performed at the 10-ID-B beamline of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). Data reduction, processing and subsequent modeling were performed using the Demeter XAS software package [18]. Modeling of the EXAFS data of Bi\(_2\)O\(_2\)(CO\(_3\))\(_x\)Cl\(_y\) was performed using Bi–O, Bi–C and Bi–Bi backscattering paths from the crystal structure of Bi\(_2\)O\(_2\)CO\(_3\) [19], while the Bi–Cl contributions were generated from the optimized structure generated from the DFT calculations. All EXAFS fitting was performed using an \( S_0^2 \) value of 0.868, which were obtained by modeling the EXAFS of a reference Bi foil \((L_3\text{-edge at }13,419 \text{ eV}).\) To minimize error in CN and NND values, Debye–Waller factors were optimized in initial rounds of EXAFS fitting and then held constant.

### 2.7 DFT Calculations

All computation studies were performed using density functional theory (DFT) implemented in the Vienna Ab-initio Simulation Package (VASP) code in this study [20, 21]. For the effects of electron–electron exchange and correlation, the Perdew–Burke–Ernzerhof (PBE) functional at the generalized gradient approximation (GGA) level was employed [22]. The projected augmented wave (PAW) potentials were used throughout for ion–electron interactions [23], with the \( 5d^{10}6s^26p^3, 2s^22p^2, 2s^2p^4, 3s^23p^5 \) and \( 1s^1 \) treated as valence electrons of Bi, C, O, Cl and H, respectively. The plane-wave cutoff of 520 eV was set for all the computations. The \((1 \times 2)\) clean \( \{001\} \) facetted Bi\(_2\)O\(_2\)CO\(_3\) was modeled by a 14-atomic layer slab separated by a vacuum layer of 20 Å in this study. When geometries of all structures were optimized, top seven layers of the surfaces including adsorbate were relaxed, while the bottom seven layers were fixed. The gamma-centered Monkhorst–Pack \( k \)-point meshes with a reciprocal space resolution of \( 2\pi \times 0.04 \text{ Å}^{-1} \) were utilized for structural optimization. For the calculations on CO\(_2\) and formic acid molecules, a \((20 \times 20 \times 20)\) Å\(^3\) unit cell and a \( \Gamma \)-only \( k \)-point grid were used. All atoms were allowed to relax until the Hellmann–Feynman forces were smaller than 0.01 eV Å\(^{-1}\), and the convergence criterion
for the electronic self-consistent loop was set to 10\(^{-5}\) eV. The adsorption energy of each adsorbate \([\Delta E (eV/n)]\) was calculated as follows:

\[
\Delta E = \frac{1}{n} \left( E_{ad/surf} - E_{surf} - nE_{ad} \right)
\]

where \(E_{ad}\), \(E_{surf}\) and \(nE_{ad}\) are the energies of an adsorbate, the clean \{001\} facet and the surface with adsorbates, respectively. And \(n\) is the number of adsorbates on the surface.

Based on computational hydrogen electrode (CHE) model [24, 25], each electrochemical reaction step can be regarded as a simultaneous transfer of the proton–electron pair as a function of the applied potential. The reaction mechanism of \(\text{CO}_2\) reduction should consist of the following elementary reactions:

\[
\text{CO}_2(g) + * + \text{H}^+(aq) + e^- \rightarrow *\text{COOH}
\]

\[
*\text{COOH} + \text{H}^+(aq) + e^- \rightarrow \text{HCOOH} + *
\]

\[
\text{CO}_2(g) + * + \text{H}^+(aq) + e^- \rightarrow *\text{OCHO}
\]

\[
*\text{CHO} + \text{H}^+(aq) + e^- \rightarrow \text{HCOOH} + *
\]

where * means the corresponding surface and adsorbed states. The free energy for all intermediate states and non-adsorbed gas-phase molecule is calculated as:

\[
G = E_{\text{elec}} + E_{\text{ZPE}} + \int C_p dT - TS
\]

where the \(E_{\text{elec}}\) is the electronic energy obtained from DFT calculation; \(E_{\text{ZPE}}\) is the zero-point vibrational energy estimated by harmonic approximation; \(\int C_p dT\) is the enthalpic correction and \(TS\) is the entropy. Here, reported values of \(E_{\text{ZPE}}\) and \(\int C_p dT\) and \(TS\) are adopted [24]. The solvation effect has been considered for *COOH by stabilizing 0.25 eV [24].

### 3 Results and Discussion

#### 3.1 Synthesis and Characterization of Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\)

In this work, Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\) was synthesized by direct electrochemical conversion of the pre-synthesized BiOCl under operando \(\text{CO}_2\) RR conditions (Fig. 1a). The BiOCl nanosheets (BiOCl-NSs) were firstly synthesized as the precursor via a one-pot hydrothermal method [26]. The X-ray diffraction (XRD) pattern of the as-synthesized BiOCl-NSs (Fig. S1) can be indexed to the tetragonal BiOCl (PDF No. 06-0249). The Raman spectrum (Fig. S2) displays two strong peaks centered at 143 and 199 cm\(^{-1}\), assignable to \(A_{1g}\) (external) and \(A_{2g}\) (internal) Bi–Cl vibration modes, respectively, while the weak peak at 400 cm\(^{-1}\) can be attributed to \(B_{1g}\) mode [27]. The atomic force microscopy (AFM) and field-emission scanning electron microscopy (FE-SEM) images (Fig. S3a, b) disclose that the obtained BiOCl-NSs are octagonal shaped with sizes between 600 and 800 nm and thicknesses of ~150 nm. The high-resolution inverse fast Fourier transformation transmission electron microscopy (IFFT-TEM) image perpendicular to the nanosheet plane (Fig. S3c) reveals lattice spacings of 2.75 and 2.75 Å with an interplanar angle of 90°, corresponding to the (110) and (110) facets of BiOCl. The selected area electron diffraction (SAED) pattern (Fig. S3d) coincides to the diffraction pattern of the single crystal BiOCl \((k,l,m)\) from [001] zone axis. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding energy-dispersive X-ray spectroscopy (EDX) elemental mapping images confirm the homogeneous distribution of Bi, O and Cl throughout the entire BiOCl-NSs (Fig. S3e).

The as-synthesized BiOCl-NSs were then immobilized onto a conductive carbon paper substrate \((1.0 \times 1.0 \text{ cm}^2)\) with a loading density of 2.0 mg cm\(^{-2}\) (Fig. S4) and subject to \(-0.8\) V (vs RHE) for 2 h in \(\text{CO}_2\)-saturated 0.5 M KHCO\(_3\) solution to electrochemically convert the loaded BiOCl-NSs into Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\). The XRD pattern (Fig. 1b) of the resultant Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\) can be assigned to the tetragonal phased Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\) (PDF No. 41–1488). The Raman spectrum (Fig. 1c) displays two strong peaks at 163 and 1068 cm\(^{-1}\), attributable to the external vibration of Bi\(_2\)O\(_2\)CO\(_3\) crystal and the \(\nu_1\) mode of the intercalated \(\text{CO}_2^{2–}\) between the \(\text{BiO}_2^{2+}\) planes [28, 29]. Raman peak at 182 cm\(^{-1}\) could be assigned to the \(A_{1g}\) mode of the intercalated \(\text{Cl}^-\) in the interlayer [29, 30]. The FE-SEM and AFM images (Figs. 1d and S5) unfold that Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\) possesses a sheeted structure with lateral sizes of 600–800 nm and thicknesses of 130–140 nm. The TEM image (Fig. 1e) shows that Bi\(_2\)O\(_2\)(CO\(_3\))\(_3\)Cl\(_y\) is formed by multiple thin-layer structures with “doughnut-like” shape, resulting from the substitution of chloride by carbonate. The SAED pattern normal to the nanosheets

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(inset of Fig. 1e) manifests the reflections of Bi$_2$O$_2$CO$_3$ (k00 and 0l0, k = l = n) with [001] zone axis. The high-resolution TEM image (HRTEM, Fig. 1f) displays a lattice spacing of 0.273 nm, corresponding to Bi$_2$O$_2$CO$_3$ (110) plane, which is also confirmed by the high-resolution IFFT-HRTEM image (Fig. 1g). The HAADF-STEM image and the corresponding EDX elemental mapping (Fig. 1h) unveil the homogenously distributed Bi, O, C and Cl. The EDX estimated Bi/Cl atomic ratio in Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ is 17.7:1 (Fig. S6), significantly higher than that of BiOCl (1.2:1), confirming the presence of Cl in Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$.

The X-ray photoelectron spectroscopy (XPS) analysis was then carried out. The high-resolution XPS Bi 4f spectra (Fig. 2a) confirm the presence of Bi$^{3+}$ and Bi–O
bonds (160.0 and 165.3 eV) [31] in BiOCl. The Bi$^{3+}$ peaks of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ show a negative shift of 0.26 eV, consistent with that of reported Bi$_2$O$_2$CO$_3$ [32]. Figure 2b shows the high-resolution XPS O 1s spectra of BiOCl and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. The former could be deconvoluted into the binding energy peaks assignable to the Bi–O lattice O (530.8 eV), the surface adsorbed hydroxyl (~531.9 eV) and O species in Nafion (536.3, 533.3 and 531.9 eV) [33, 34], while the deconvoluted binding energy peaks at 530.2 and 531.0 eV from the later are ascribed to the Bi–O lattice O and C=O, respectively [35, 36]. The lattice O peaks in Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ shifted to lower energies due to the substitution of chloride by carbonate. The two binding energy peaks at 199.2 and 200.8 eV assignable to Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ can be deconvoluted from the high-resolution XPS Cl 2p spectra of both BiOCl and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ (Fig. 2c), indicating the presence of the lattice Cl$^{-}$ [37]. Notably, a Bi/Cl atomic ratio of 61.5:1 is determined from the XPS Cl 2p spectrum of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ (Fig. S7), confirming the presence of chemically bonded Cl on the surface of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$.

The X-ray absorption spectroscopy (XAS) measurements were then conducted to probe the electronic structure and local atomic environments. The O K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra of BiOCl, Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and reference samples are shown in Fig. 2d. The observed binding energy peaks at 532.0 and 537.0 eV from Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ are assignable to the hybridization of O 2p with Bi 6 s orbitals [38, 39], while the binding energy peak at 534 eV corresponds to the π* C=O transition, indicating the presence of lattice carbonyl oxygen species [40]. The displayed binding energy peaks at 539.4 and 543.2 eV in the spectrum of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ are ascribed to the non-equivalent σ* C–O bonds in the carboxylic group originated from the adsorbed carbonate [41]. Based on the C K-edge NEXAFS spectra of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and reference samples (Fig. 2e), the binding energy peak at 289.5 eV can be attributed to the σ* states of C–O [41], while the peaks at 297.2 and 299.8 eV are assignable to the σ* C=O resonances associated with the presence of carbonate species [42]. It is to note that the O K-edge and C K-edge NEXAFS spectra obtained from Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ exhibit very similar characteristics, implying that the crystal structure of Bi$_2$O$_2$CO$_3$ in Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ is not noticeably altered by the presence of Cl$^{-}$. According to the Bi L$_{3}$-edge X-ray absorption near-edge structure (XANES) spectra (Fig. 2f), the same valence states of Bi$^{3+}$ exist in BiOCl, Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. Figure 2g shows the k$^2$-weighted Fourier transformed Bi L$_{2,3}$-edge extended X-ray absorption fine structure (k$^2$-weighted FT-EXAFS) spectra of Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. The peaks at 1.74, 2.33 and 3.58 Å assignable to the Bi–O and Bi–Bi bonds in the (BiO)$_2^{2+}$ ab plane are observed from both Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$, indicating an identical (BiO)$_2^{2+}$ ab plane in both Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. The spectrum of Bi$_2$O$_2$CO$_3$ shows a peak at 2.93 Å, corresponding to the interactions of Bi in (BiO)$_2^{2+}$ ab plane with the intercalated CO$_3^{2−}$ between the (BiO)$_2^{2+}$ ab plane layers (the interlayer). Notably, for Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$, the peak is shifted to 3.01 Å, implying the differences in the interactions of Bi in (BiO)$_2^{2+}$ ab plane with the interlayer anions due to the presence of the intercalated Cl$^{-}$ in the interlayer of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. The fittings of the Bi L$_{3}$-edge k$^2$-weighted FT-EXAFS spectra of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and Bi$_2$O$_2$CO$_3$ in R space and k space were then performed (Figs. 2h, S8 and Table S2) [43]. It unveils that the spectrum of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ fits well with Bi$_2$O$_2$CO$_3$ and Bi–Cl path, confirming the presence of the intercalated Cl$^{-}$ in the interlayer. The coordination numbers (CNs) of Bi–O in the first coordination sphere of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and Bi$_2$O$_2$CO$_3$ are 2.34 at 2.22 Å and 2.27 at 2.24 Å, respectively, further confirming an almost unchanged (BiO)$_2^{2+}$ ab plane coordination environment. For Bi$_2$O$_2$CO$_3$, a Bi–C CN of 1.75 at 3.36 Å represents the interactions between the Bi atoms in the (BiO)$_2^{2+}$ ab plane and the intercalated CO$_3^{2−}$ in the interlayer. For Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$, the measured Bi–C CN of 1.51 at 3.38 Å indicates a reduction in the Bi–C CN, which is closely approximated to the dropped Bi–C CN, unambiguously confirming the presence of the intercalated Cl$^{-}$ between (BiO)$_2^{2+}$ ab plane layers in Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. A likely Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ structure is shown in Fig. 2i. The above results confirm that under −0.8 V (vs RHE) cathodic potential in CO$_2$-saturated 0.5 M KHCO$_3$ solution for 2 h, the BiOCl-NSs are electrochemically reduced into Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$.

### 3.2 Operando Converting BiOCl into Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$

It is known that both of the tetragonal BiOCl and Bi$_2$O$_2$CO$_3$ crystals (Fig. S9) belong to the Sillén crystal family, featuring a matlockite-type positively charged...
(BiO)$_2^{2+}$ planes layer structure stacking between the negatively charged bichloride and “standing-on-end” CO$_3^{2-}$ anions slabs, respectively. Comparing to the $d$ spacing of \{001\} faceted BiOCl along the $c$ axis (7.83 Å), the $d$ spacing of \{002\} faceted Bi$_2$O$_2$CO$_3$ is markedly reduced to 6.84 Å. Therefore, under apt cathodic potentials, due to the layer structure similarity, and the apparently decreased $d$ spacing of \{002\} faceted Bi$_2$O$_2$CO$_3$, the transformation of BiOCl to Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ could occur via the intercalative substitution of the interlayer Cl$^-$ with CO$_3^{2-}$ through a glide of the neighboring (BiO)$_2^{2+}$ ab planes along [100] and [010] directions with the translational distances of $\frac{1}{2} a$ and $\frac{1}{2} b$, respectively [17]. To depict the structural evolution processes under the operando CO$_2$RR conditions, the BiOCl-NSs immobilized on the carbon fiber paper were subjected to different cathodic potentials ($E_{\text{App}}$) in CO$_2$-saturated 0.5 M KHCO$_3$ solution, and the XRD patterns were operando recorded. The XRD patterns recorded under the open circuit potential (OCP) and $E_{\text{App}} \leq -0.2$ V (Fig. 3a) are almost identical to that of the as-synthesized BiOCl (Fig. S1). The initial conversion of BiOCl to Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ occurs at $E_{\text{App}} = -0.3$ V as

![Fig. 2 High-resolution XPS spectra of a Bi 4f, b O 1s and c Cl 1s obtained from the as-synthesized BiOCl-NSs and Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$. d O K-edge spectra, e C K-edge spectra and f Bi L$_{3}$-edge spectra of BiOCl, Bi$_2$O$_2$CO$_3$, Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and referenced samples. g Bi L$_{3}$-edge $k^2$-weighted FT-EXAFS spectra of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and Bi$_2$O$_2$CO$_3$ in R space. h Fitting analysis of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ using Bi–O, Bi–C and Bi–Cl paths. i Proposed geometric configuration of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$.](https://doi.org/10.1007/s40820-022-00862-0)
indicated by the observed diffraction peak at 56.9° corresponding to (123) faceted Bi$_2$O$_2$CO$_3$. When $E_{\text{App}}$ is increased from $-0.3$ to $-0.7$ V, although the recorded XRD patterns are still dominated by the diffraction patterns of BiOCl, the progress of converting BiOCl to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ is evidenced by the progressively increased intensities of Bi$_2$O$_2$CO$_3$ diffraction peaks and the accompanied decrease in the intensities of BiOCl diffraction peaks. With $E_{\text{App}} = -0.8$ V, all recorded diffraction peaks belong to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ (PDF No. 41-1488), signifying the complete conversion of BiOCl to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$. The structural evolution and the time required to completely convert BiOCl to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ under $E_{\text{App}} = -0.8$ V were subsequently investigated (Fig. S10). As can be seen, BiOCl is fully covered to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ within 60 min under $E_{\text{App}} = -0.8$ V. As disclosed in Fig. 3a, Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ remains as the sole product when $-0.8$ V $\leq E_{\text{App}} \leq -1.0$ V. With $E_{\text{App}} = -1.1$ V, the bismuth in Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ is partially reduced to the metallic phased Bi$^0$ as evidenced by the appearance of the diffraction peaks assignable to the rhombohedral phased Bi$^0$ (PDF No. 05–0519). With $E_{\text{App}} = -1.2$ V, all of the recorded diffraction peaks belong to the rhombohedral phased Bi$^0$, confirming the ultimate conversion of Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ to the metallic Bi$^0$ phase. As shown in Fig. S11, the BiOCl-derived Bi$^0$ at $E_{\text{App}} = -1.2$ V is formed by the aggregated Bi$^0$ NSs with the exposed {001} facets. Notably, the required cathodic potential to convert Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ to Bi$^0$ is more negative than those reported potentials to reduce Bi$_2$O$_2$CO$_3$ to Bi$^0$ [44], [Lv, 2017 #1765] inferring a superior electrochemical stability of Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ over Bi$_2$O$_2$CO$_3$, which might be attributed to the presence of Cl$^-$ in Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$. To confirm this, the pure tetragonal phased Bi$_2$O$_2$CO$_3$ nanosheets (Figs. S12–S14) were synthesized by a wet-chemistry method [43] and subjected to different cathodic potentials in CO$_2$-saturated 0.5 M KHCO$_3$ solution. Figure 3b shows the operando recorded XRD patterns. The formation Bi$^0$ occurs at $E_{\text{App}} = -0.6$ V, while the Bi$_2$O$_2$CO$_3$ is fully converted to the rhombohedral phased metallic Bi$^0$ (PDF No. 05-0519) at $E_{\text{App}} = -0.8$ V, confirming that the presence of Cl$^-$ in Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ is responsible for the improved electrochemical stability. It is noteworthy that compared to the characteristic diffraction peaks of Bi$_2$O$_2$CO$_3$, all of the recorded characteristic diffraction peaks from Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ are shifted slightly toward lower angles (Fig. S15), indicating an expended $d$ spacing in Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ due to the presence of Cl$^-$ in the interlayer. The above operando XRD studies unveil that the electrochemical conversion of BiOCl to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ is realized by the cathodic potential-promoted anion-exchange in the interlayer between the (BiO)$_2^{2+}$ $ab$ planes.

To further elaborate the electrochemical conversion pathway, the operando potential-dependent Raman spectra of BiOCl immobilized on the carbon fiber paper were recorded under different cathodic potentials in CO$_2$-saturated 0.5 M KHCO$_3$ solution (Fig. 3c). Under the OCP and $E_{\text{App}} \leq -0.3$ V conditions, the recorded spectra are almost identical to that of the as-synthesized BiOCl-NSs (Fig. S2). With $E_{\text{App}} = -0.4$ V, the characteristic peaks of BiOCl at 143 ($A_1^g$) and 199 cm$^{-1}$ ($A_1^g$) are markedly reduced and disappeared, respectively, which are accompanied by the appearance of a new peak at 182 cm$^{-1}$ that might be assigned to the $A_{1g}$ mode of the intercalated Cl$^-$ in the interlayer, although this could be complicated by the reduced crystal symmetry due to the disorder or free rotation of CO$_2$ in the interlayer [29, 30]. These observed changes in the Raman spectrum signify the initial conversion of BiOCl to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$ at $E_{\text{App}} = -0.4$ V, consistent with the operando XRD observation shown in Fig. 3a. At $E_{\text{App}} = -0.8$ V, two new peaks at 163 and 1068 cm$^{-1}$ attributed to the external vibration of Bi$_2$O$_2$CO$_3$ crystal and the $\nu_1$ mode of CO$_2$ anions between the (BiO)$_2$ planes appear, signifying the complete conversion of BiOCl to Bi$_2$O$_2$(CO$_3$)$_y$Cl$_x$. Within $-0.8$ V $\leq E_{\text{App}} \leq -1.0$ V, the peak at 182 cm$^{-1}$ ($A_{1g}$ mode) is rapidly decreased, while the peaks at 163 and 1068 cm$^{-1}$ are evolved and intensified, which are likely due to the changes in the local atomic symmetry rather than the crystal cell parameters because of the unchanged operando XRD patterns within the same potential range (Fig. 3a). It is known that the high-intensity Raman bands between 150 and 200 cm$^{-1}$ normally correspond to the out-of-plane lattice vibrations of the Bi atoms perpendicular to the (BiO)$_2$ layers [45]. Because the phonon frequencies are sensitive to the dopant-induced asymmetry and the interlayer thickness, therefore, the blueshifted phonons from 182 to 163 cm$^{-1}$ could be resulted from the suppressed vibrations of the (BiO)$_2$ layers along $c$ direction due to the replaced Cl$^-$ by CO$_2$ at relatively high cathodic potentials. The characteristic Raman peaks of Bi$_2$O$_2$CO$_3$ at 163 and 1068 cm$^{-1}$ are dramatically decreased under $E_{\text{App}} = -1.1$ V and vanished.
at $E_{\text{App}} = -1.2$ V due to the formation of metallic Bi$^0$, consistent with the operando XRD observations. For comparative purpose, the operando potential-dependent Raman spectra of the pure tetragonal phased Bi$_2$O$_2$CO$_3$ nanosheets were obtained (Fig. 3d). When $E_{\text{App}} \leq -0.5$ V, the peak at 182 cm$^{-1}$ associating with the $A_{1g}$ mode of the intercalated Cl$^-$ in the CO$_3$$^{2-}$ slab is absent, while the characteristic Raman peaks of Bi$_2$O$_2$CO$_3$ at 163 and 1068 cm$^{-1}$ are apparent, however, rapidly extinct when $E_{\text{App}} \geq -0.6$ V due to the formation of metallic Bi$^0$, consistent with the operando

Fig. 3  a, b Operando XRD patterns of the as-synthesized BiOCl-NSs and Bi$_2$O$_2$CO$_3$ recorded from CO$_2$-saturated 0.5 M KHCO$_3$ solution under different cathodic potentials. c, d Operando Raman spectra of the as-synthesized BiOCl-NSs and Bi$_2$O$_2$CO$_3$ recorded from CO$_2$-saturated 0.5 M KHCO$_3$ solution under different cathodic potentials
XRD observations shown in Fig. 3b. This further confirms that compared to the chloride-free Bi$_2$O$_2$CO$_3$, the reduction of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ to metallic Bi$^0$ requires a much higher cathodic potential due to presence of the intercalated Cl$^-$ in the CO$_2$-slab, signifying a noticeably improved electrochemical stability. These *operando* Roman studies further suggest that the conversion of BiOCl to Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ is achieved by the cathodic potential-promoted anion-exchange in the interlayer.

### 3.3 CO$_2$RR Performance

All electrochemical measurements were performed using a three-electrode electrochemical system with Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ or Bi$_2$O$_2$CO$_3$ working electrode in CO$_2$- or Ar-saturated 0.5 M KHCO$_3$ solution. When $E_{\text{App}} > -0.5$ V (vs EHE), the linear sweep voltammetry (LSV) responses of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ in CO$_2$-saturated solution display higher cathodic current densities than that obtained from the Ar-saturated solution (Fig. S16), indicating a superior electrocatalytic activity of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ toward CO$_2$RR. The potentiostatic experiments were then performed under different cathodic potentials to examine the electrocatalytic CO$_2$RR activity and selectivity. Figure 4a shows the chronoamperometric curves of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ from the CO$_2$-saturated 0.5 M KHCO$_3$ solution. The reaction products in gaseous and aqueous phases were qualitatively identified and quantitatively determined by the gas chromatography (GC) and nuclear magnetic resonance (NMR). For all cases investigated, H$_2$ is identified as the sole product in the gaseous phase, while the formate is found to be the sole product in the aqueous phase. The NMR determined formate concentrations (Figs. S17 and S18) corresponding to the chronoamperometric curves shown in Fig. 4a were used to calculate the corresponding $J_{\text{HCOO}^-}$ and $J_{\text{HCOO}^-}$ values. Figure 4b shows the plot of $J_{\text{HCOO}^-}$ against $E_{\text{App}}$. For both Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ and Bi$_2$O$_2$CO$_3$, an increase in $E_{\text{App}}$ leads to an increase in $J_{\text{HCOO}^-}$. For a given $E_{\text{App}}$, the observed $J_{\text{HCOO}^-}$ from Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ is higher than that observed from Bi$_2$O$_2$CO$_3$, implying a superior CO$_2$RR activity of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ over Bi$_2$O$_2$CO$_3$. At $E_{\text{App}} = -0.8$ V, the $J_{\text{HCOO}^-}$ attained by Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ is 18.4 mA cm$^{-2}$, higher than that of Bi$_2$O$_2$CO$_3$ (14.2 mA cm$^{-2}$). Figure 4c shows the plot of $J_{\text{HCOO}^-}$ (derived from Fig. 4a) against $E_{\text{App}}$. For Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$, an increase in $E_{\text{App}}$ from −0.4 to −0.6 V leads to a rapidly increased $J_{\text{HCOO}^-}$ from 79.2 to 96.2%, and further increasing $E_{\text{App}}$ to −0.8 V leads to an increased $J_{\text{HCOO}^-}$ to 97.9%. $J_{\text{HCOO}^-}$ remains almost unchanged when $E_{\text{App}}$ is further increased to −1.0 V, while the corresponding $J_{\text{HCOO}^-}$ is increased to 40.5 mA cm$^{-2}$ (Fig. 4b). Based on the *operando* XRD and Raman observations (Fig. 3a, c), the formation of the metallic phased Bi$^0$ will not occur with $E_{\text{App}} \leq -1.0$ V, therefore, the observed changes in $J_{\text{HCOO}^-}$ from the potential range of −0.4 V $\leq E_{\text{App}} \leq -1.0$ V reflect the influence of potential on CO$_2$RR selectivity of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$. Although Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ is partially converted to metallic Bi–NSs within −1.0 V $\leq E_{\text{App}} \leq -1.2$ V (Fig. 3a, c), the high $J_{\text{HCOO}^-}$ can still be attained due to the electrocatalytic activity of Bi$^0$ toward CO$_2$RR under high cathodic potentials [17]. When $E_{\text{App}} > -1.2$ V, the observed decrease in $J_{\text{HCOO}^-}$ is due to the intensified competition from HER [7]. Interestingly, for pure Bi$_2$O$_2$CO$_3$, a rapidly increased $J_{\text{HCOO}^-}$ from 65.5 to 77.5% is observed when $E_{\text{App}}$ is increased from −0.4 to −0.6 V and reached a maxima $J_{\text{HCOO}^-}$ of 83.0% at $E_{\text{App}} = -0.7$ V, where Bi$_2$O$_2$CO$_3$ is partially converted to the metallic Bi$^0$. With −0.8 V $\leq E_{\text{App}} \leq -1.2$ V, Bi$_2$O$_2$CO$_3$ is fully converted to the metallic Bi$^0$ and the slightly decreased $J_{\text{HCOO}^-}$ reflects the influence of potential on CO$_2$RR selectivity of metallic Bi$^0$ rather than that of Bi$_2$O$_2$CO$_3$. When $E_{\text{App}} > -1.2$ V, $J_{\text{HCOO}^-}$ is rapidly decreased due to the intensified competition from HER.

The chronoamperometric stability of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ (Fig. 4d) was evaluated over a 20 h period in CO$_2$-saturated 0.5 M KHCO$_3$ solution at $E_{\text{App}} = -0.8$ V vs RHE. While $J_{\text{HCOO}^-}$ of ~95% is well retained, a 12.1% increase in the cathodic current density is observed, indicating an increased $J_{\text{HCOO}^-}$. Interestingly, when the used electrolyte is replaced by the fresh one, an almost identical chronoamperometric curve is obtained with ~12% increase in the cathodic current density at 20 h, indicating an excellent long-term stability of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ [46]. The excellent electrocatalytic stability of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ can be attributed to its excellent structural stability as evidenced by the almost unchanged XRD pattern (Fig. S19), Raman spectra (Fig. S20), as well as SEM and TEM images (Fig. S21) of Bi$_2$O$_2$(CO$_3$)$_3$Cl$_y$ after the chronoamperometric stability test. The chronoamperometric stability of Bi$_2$O$_2$CO$_3$ was also evaluated at $E_{\text{App}} = -0.8$ V vs RHE (Fig. S22). Over a 20 h testing period, $J_{\text{HCOO}^-}$ is decreased from 86.2 to 80.0%, while the cathodic current density is increased from
12.5 to 14.2 mA cm$^{-2}$. However, after the chronoamperometric stability test, the pure tetragonal phased Bi$_2$O$_2$CO$_3$ is fully converted to the metallic phased Bi$^6$ (Figs. S23–S26). The stability test result confirms that Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ fabricated under operando CO$_2$RR conditions possesses excellent stability.

### 3.4 DFT Calculations

It is known that electrocatalytic CO$_2$RR to HCOOH has normally proceeded via a proton-coupled electron transfer (PCET) step to form *COOH or *OCHO intermediates and followed by another PCET step to generate HCOOH [47]. It

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**Fig. 4**  

- **a** Chronoamperometric curves of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ recorded from CO$_2$-saturated 0.5 M KHCO$_3$ solution under different cathodic potentials.  
- **b, c** Plots of HCOOH partial current density and Faradic efficiency against cathodic potential for Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ and Bi$_2$O$_2$CO$_3$-catalyzed CO$_2$RR.  
- **d** Chronoamperometric curves and FE$_{HCOOH}$ of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$ at −0.8 V versus RHE.  
- **e** Free energy diagrams of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$- and Bi$_2$O$_2$CO$_3$-catalyzed CO$_2$ reduction to HCOOH.  
- **f** PDOS plots of Bi$_2$O$_2$(CO$_3$)$_x$Cl$_y$- and Bi$_2$O$_2$CO$_3$-catalyzed CO$_2$ reduction to HCOOH.
is also known that the CO$_2$RR pathway depends strongly on the adsorption energy of the intermediates [48]. DFT calculations were therefore carried out to determine the preferable intermediates of the pure tetragonal phased Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$-catalyzed CO$_2$ reduction to HCOOH. Our DFT calculations unveil that $^\circ$OCHO intermediate can preferentially adsorb on the [001] faceted Cl-free Bi$_2$O$_2$CO$_3$ surface [49] with an adsorption free energy ($\Delta G_{\text{OCHO}}$) of $-2.67$ eV (Fig. S27a), while no stable structure of $^\circ$COOH intermediate adsorbed on the [001] faceted Cl-free Bi$_2$O$_2$CO$_3$ can be obtained. These results imply that the pure tetragonal phased Bi$_2$O$_2$CO$_3$-catalyzed CO$_2$ reduction to HCOOH has proceeded via a $^\circ$OCHO intermediate pathway. In contrast, our initial DFT calculations are failed to obtain a stable structure of $^\circ$OCHO intermediate adsorbed on Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ surface. Nonetheless, further DFT calculations unveil that the $^\circ$COOH intermediate is apt to absorb to the Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ surface with a $\Delta G_{\text{COOH}}$ of $-1.25$ eV (Fig. S27b), inferring that the Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$-catalyzed CO$_2$ reduction to HCOOH has proceeded via a $^\circ$COOH intermediate pathway. Figure 4e illustrates the free energy diagrams of Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$-catalyzed CO$_2$ reduction to HCOOH. During the 1st PCET step, the formation of $^\circ$OCHO on Bi$_2$O$_2$CO$_3$ surface and $^\circ$COOH on Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ surface is exothermic. During the 2nd PCET step, the formation of $^\circ$HCOOH on Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ is exothermic, while on Bi$_2$O$_2$CO$_3$ is endothermic. The desorption of $^\circ$HCOOH from Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ to form HCOOH are energetically uphill. However, the desorption of $^\circ$HCOOH from Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ requires 2.56 eV to proceed, which is 0.13 eV lower than that of Bi$_2$O$_2$CO$_3$ (2.69 eV), indicating a better kinetic activity of Bi in Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$, corresponding to a LUMO potential of $-2.3$ eV. It is known that for semiconductor electrodes, the reduction reaction takes place via the injection of electrons into LUMO. Therefore, the LUMO potential corresponds to the minimum required cathodic potential for electron injection. As illustrated in Fig. S28, compared to Bi$_2$O$_2$CO$_3$, the higher LUMO potential of Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ infers that a higher cathodic potential is required to convert Bi$^{3+}$ in Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ to metallic Bi$^0$, which explains the superior electrochemical stability of Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$ over Bi$_2$O$_2$CO$_3$ under CO$_2$RR conditions.

4 Conclusions

In summary, we reported an approach to electrochemically convert bismuth oxychloride (BiOCl) into chloride-containing bismuth subcarbonate (Bi$_2$O$_2$(CO$_3$)$_2$Cl$_4$) under operando CO$_2$RR conditions. We demonstrated that the operando synthesis is an effective strategy to enhance the electrochemical stability of bismuth-based electrocatalysts. The exemplified approach in this work could be widely applicable to enhance the electrochemical stabilities of other electrocatalysts for other reactions.

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