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## Formation of toroidal $\text{Li}_2\text{O}_2$ in non-aqueous Li–O<sub>2</sub> batteries with $\text{Mo}_2\text{CT}_x$ MXene/CNT composite†

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Due to the growing demand for high energy density devices, Li–O<sub>2</sub> batteries are considered as a next generation energy storage system. The battery performance is highly dependent on the Li<sub>2</sub>O<sub>2</sub> morphology, which arises from formation pathways such as the surface growth and the solution growth models. Thus, controlling the formation pathway is important in designing cathode materials. Herein for the first time, we controlled the Li<sub>2</sub>O<sub>2</sub> formation pathway by using Mo<sub>2</sub>CT<sub>x</sub> MXene on a catalyst support. The cathode was fabricated by mixing the positively charged CNT/CTAB solution with the negatively charged Mo<sub>2</sub>CT<sub>x</sub> solution. After introducing Mo<sub>2</sub>CT<sub>x</sub>, important battery performance metrics were considerably enhanced. More importantly, the discharge product analysis showed that the functional groups on the surface of Mo<sub>2</sub>CT<sub>x</sub> inhibit the adsorption of O<sub>2</sub> on the cathode surface, resulting in the formation of toroidal Li<sub>2</sub>O<sub>2</sub> via the solution growth model. It was supported by density functional theory (DFT) calculations that adsorption of O<sub>2</sub> on the Mo<sub>2</sub>CT<sub>x</sub> surface is implausible due to the large energy penalty for the O<sub>2</sub> adsorption. Therefore, the introduction of MXene with abundant functional groups to the cathode surface can provide a cathode design strategy and can be considered as a universal method in generating toroidal Li<sub>2</sub>O<sub>2</sub> morphology.

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### Introduction

Li–O<sub>2</sub> batteries have been considered to be a promising candidate for high energy density energy storage systems due to their extremely high energy density (~3500 W h kg<sup>-1</sup>), which is far higher than that of current Li-ion batteries.<sup>1</sup> The typical redox reaction mechanism of the Li–O<sub>2</sub> battery is the formation and decomposition of lithium peroxide (Li<sub>2</sub>O<sub>2</sub>); during discharge, an oxygen reduction reaction (ORR) occurs on the surface of the cathode electrode to produce Li<sub>2</sub>O<sub>2</sub> as a discharge product, and during charge, electrochemical decomposition of the produced Li<sub>2</sub>O<sub>2</sub> into Li<sup>+</sup> and O<sub>2</sub> occurs, that is oxygen evolution reaction (OER).<sup>2</sup>

Recent studies revealed that comprehension of electrochemistry and the chemistry behind the Li<sub>2</sub>O<sub>2</sub> formation are crucial in determining the Li–O<sub>2</sub> battery performances.<sup>4</sup> Specifically, there are two Li<sub>2</sub>O<sub>2</sub> formation models: (i) surface growth model and (ii) solution growth model.<sup>4</sup> In the surface growth model, since the nucleation of Li<sub>2</sub>O<sub>2</sub> occurs on the surface of the cathode, the morphology of the deposited Li<sub>2</sub>O<sub>2</sub> is a thin film type, resulting in small discharge capacity due to the small amount of produced Li<sub>2</sub>O<sub>2</sub> but low OER overpotential due to the close contact of the thin film. In the solution growth model, since the nucleation of Li<sub>2</sub>O<sub>2</sub> occurs in the solution via the disproportionation reaction of the soluble LiO<sub>2</sub> intermediate, the resultant morphology of Li<sub>2</sub>O<sub>2</sub> is a toroidal structure, which leads to high discharge capacity due to the large amount of produced Li<sub>2</sub>O<sub>2</sub> but a high OER overpotential due to the large particle size of toroidal Li<sub>2</sub>O<sub>2</sub>.<sup>4</sup> Thus, the formation of Li<sub>2</sub>O<sub>2</sub> highly influences the electrochemical properties of the Li–O<sub>2</sub> batteries.

One of the most effective strategies in controlling and changing Li<sub>2</sub>O<sub>2</sub> formation pathway is selecting cathode materials with different O<sub>2</sub> adsorbability. It is highly suggested that thin film type Li<sub>2</sub>O<sub>2</sub> morphology can be obtained by using a cathode with high O<sub>2</sub> affinity (e.g. Co<sub>3</sub>O<sub>4</sub> and Mo<sub>2</sub>C) via the surface growth model. On the other hand, it is recommended that toroidal Li<sub>2</sub>O<sub>2</sub> can be achieved by using the cathode with low O<sub>2</sub> affinity via the solution growth model.<sup>5</sup>

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Here, we used MXene for the first time to control the O<sub>2</sub> adsorbability of the cathode, which is attributed to the surface functional groups with high coverage. MXenes are a new family of two-dimensional (2D) transition metal carbides,<sup>6</sup> and considered to be one of the most promising materials for energy storage systems due to their high electrical conductivity, rapid diffusion of ions and molecules, high specific surface area, and hydrophilic surfaces.<sup>7</sup> The general formula of MXene is M<sub>n+1</sub>X<sub>n</sub>T<sub>x</sub> ( $n = 1-3$ ), where M stands for transition metals, X stands for nitrogen or/and carbon, and consequently, there are diverse compositions of MXenes (e.g. Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, Ti<sub>2</sub>CT<sub>x</sub>, Zr<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, Sc<sub>4</sub>N<sub>3</sub>T<sub>x</sub>, and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>) with T<sub>x</sub> representing the surface termination groups (e.g. oxygen, hydroxyl and fluorine), which fully cover the outer surface.<sup>8</sup> In general, preparing materials with high surface coverage is challenging because it is difficult to introduce surface functionality in significantly high concentrations. However, MXenes are covered by surface termination groups with extraordinarily high surface coverage,<sup>9</sup> which is responsible for its uniqueness. We found that MXene plays an important role in determining Li<sub>2</sub>O<sub>2</sub> formation pathway in non-aqueous Li–O<sub>2</sub> batteries.

## Experimental

### Preparation of Mo<sub>2</sub>CT<sub>x</sub>

Mo<sub>2</sub>CT<sub>x</sub> was prepared by the method previously reported elsewhere.<sup>10</sup> Mo<sub>2</sub>CT<sub>x</sub> was synthesized by selective etching of gallium (Ga, Kojundo Korea, 99.99%) atoms from Mo<sub>2</sub>Ga<sub>2</sub>C using concentrated hydrofluoric acid (HF, Junsei, 40%). Mo<sub>2</sub>Ga<sub>2</sub>C was prepared by a solid–liquid reaction between Mo<sub>2</sub>C and Ga, in a molar ratio of 1 : 8. The mixture was annealed at 850 °C for 16 hours in a vacuum furnace and cooled down to room temperature, followed by re-annealing at 850 °C for 48 hours to form Mo<sub>2</sub>Ga<sub>2</sub>C. Then, 2 g of Mo<sub>2</sub>Ga<sub>2</sub>C was placed in a polypropylene (PP) beaker with 40 ml of concentrated HF and stirred for 6 days to remove Ga atoms. The resultant powder was washed with 1 M hydrochloric acid (HCl, Daejung, 35%) and de-ionized water for several cycles until the pH of  $\approx 7$  was reached. To obtain delaminated Mo<sub>2</sub>CT<sub>x</sub>, 1 g of the powder was immersed in 10 ml of tetrabutylammonium hydroxide (TBAOH, Sigma-Aldrich, 57%) for 4 hours, then washed with DI water. 250 ml of DI water was added to the TBAOH-treated powder, and sonicated in an ice bath for 1 hour using a dismembrator. Then 40 ml of the above suspension was transferred to each centrifuge tube, and was centrifuged at 25 000 rpm for 5 min. The resultant supernatant was collected whereas the settled powder was removed.

### Preparation of CNT/Mo<sub>2</sub>CT<sub>x</sub>

50 mg of carbon nanotube (CNT) was dispersed in 100 ml of DI water with cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich) to produce a 0.5 mg ml<sup>-1</sup> solution. 140 ml of DI water was added to 14 ml of CNT solution to produce a dilute CNT solution, and was added dropwise into the delaminated Mo<sub>2</sub>CT<sub>x</sub>, obtaining a weight ratio between CNT and Mo<sub>2</sub>CT<sub>x</sub> of 7 to 3, and it was then stirred for 1 hour. Then polystyrene bead

(PS, Sigma-Aldrich, 10 wt%) was added to the above suspension to obtain the weight ratio between CNT/Mo<sub>2</sub>CT<sub>x</sub> to polystyrene bead as 1 to 10, and it was then sonicated for 30 min. The resultant suspension was vacuum filtrated with a membrane filter (Durapore, 0.22  $\mu$ m GV), and dried at 80 °C for 12 hours. The resultant electrode was peeled off from the membrane filter, and then annealed at 450 °C for 2 hours under Ar to remove PS beads.

To clarify the effect of MXene, the CNT electrode was fabricated by the same procedure with 20 ml of CNT solution but without Mo<sub>2</sub>CT<sub>x</sub>.

### Measurements

The surface and cross-sectional view of the CNT and CNT/Mo<sub>2</sub>CT<sub>x</sub> electrodes were characterized by using scanning electron microscopy (SEM, Tescan Mira 3 LMU FEG, 20 kV). The surface functional groups were identified by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific). The crystal structure of the discharged product was confirmed by X-ray powder diffractometer (XRD, Rigaku ultima IV Diffractometer) with graphite-monochromator equipped with Cu K $\alpha$  line (40 kV/40 mA). The Brunauer–Emmett–Teller (BET) surface area was measured by nitrogen adsorption/desorption at 77.3 K.

The CNT and CNT/Mo<sub>2</sub>CT<sub>x</sub> electrodes served as the cathode, which were dried at 120 °C for 12 hours under vacuum, then assembled in an argon-filled glove box using Swagelok type cells. The average mass loading of the electrode was about 0.65 mg and the size was 12 mm in diameter.

The electrolyte was 1 M lithium nitrate (LiNO<sub>3</sub>, Sigma-Aldrich) in dimethylacetamide (DMAc, Sigma-Aldrich) with water concentration <30 ppm determined by a Mettler-Toledo Karl Fischer titration. Li foil served as the anode.

Electrochemical performances were tested with a battery cycler (WBCS-3000, WonAtech) at an applied current density of 200 mA g<sub>CNT</sub><sup>-1</sup> for 5 hours and 100 mA g<sub>CNT</sub><sup>-1</sup> with 2.0 V cut-off, respectively, for cycle life and specific capacity measurements.

### Calculations

All of the first-principle calculations were performed with the Vienna *Ab Initio* Simulation Package (VASP)<sup>18</sup> with the projector augmented wave (PAW)<sup>19</sup> potentials. In order to calculate the adsorption energy of O<sub>2</sub> on the surface of  $\beta$ -Mo<sub>2</sub>C, the Perdew–Burke–Ernzerhof (PBE)<sup>20</sup> along with the dispersion force for van de Waals interactions (PBE-D3)<sup>21</sup> was utilized for exchange–correlation functional. The geometry optimizations were conducted with a maximum force criterion of 0.005 eV  $\text{\AA}^{-1}$ , energy criterion of 10<sup>-6</sup> eV per cell and cutoff energy of 520 eV. The initial unit-cells of  $\beta$ -Mo<sub>2</sub>C and Mo<sub>2</sub>C(OH)<sub>2</sub> were set with a vacuum space of 30  $\text{\AA}$  along the vertical direction of single layer of MXene with a  $\Gamma$ -centered 12  $\times$  12  $\times$  1 *k*-mesh. The (3  $\times$  3) slabs were utilized for calculating the O<sub>2</sub> adsorption energy with a  $\Gamma$ -centered 4  $\times$  4  $\times$  1 *k*-mesh. The vibrational frequency analysis are obtained by PHONOPY<sup>22</sup> code. The force constants matrix was constructed by 4  $\times$  4  $\times$  1 supercell with density functional perturbation theory.<sup>23</sup>

## Results and discussion

The schematic for fabricating the CNT/Mo<sub>2</sub>CT<sub>x</sub> cathode is described in Fig. 1. We selected carbon nanotubes (CNTs) as a catalyst support due to their excellent electrical conductivity, high mechanical strength, and facile fabrication into binder-free cathode.<sup>11</sup> Moreover, they provide a porous structure for better O<sub>2</sub> diffusion and Li<sub>2</sub>O<sub>2</sub> accommodation. It is noteworthy that Mo<sub>2</sub>CT<sub>x</sub> was used as a catalyst simply because of its good catalytic activity in catalysis field<sup>12</sup> as well as easy fabrication.<sup>10</sup>

Since CNT was dispersed with a cationic surfactant cetyltrimethylammonium bromide (CTAB), the surface of the CNTs were positively charged; whereas the surface functional groups including -O and -OH result in the negatively charged MXene surfaces. The positively charged CNT solution was added to the negatively charged Mo<sub>2</sub>CT<sub>x</sub> solution to obtain uniformly attached Mo<sub>2</sub>CT<sub>x</sub> on the surface of CNTs in a weight ratio of 3 to 7, by the electrostatic force.<sup>13</sup> The PS beads were added to the mixed solution, then the resultant solution was vacuum filtered to fabricate paper type electrode. The electrode was annealed at 450 °C to create micron-sized pores in the electrode by PS removal.

SEM image shows that CNTs are well distributed over the paper type electrode with porous structure and possess well-connected networks (Fig. 2a). After introducing MXene catalyst to the CNTs, there are small Mo<sub>2</sub>CT<sub>x</sub> particles deposited on the CNTs (see the arrows of Fig. 2b), which were confirmed by EDS mapping in Fig. S1,† in maintaining pristine CNT morphology. Inset images of Fig. 2a and b exhibit the cross-sectional views of CNT and CNT/Mo<sub>2</sub>CT<sub>x</sub> electrodes, respectively, to clarify the formation of macropores after PS calcination. It has been reported that introducing pores in the paper type electrode can improve the cycle life by preventing irreversible volume expansion of the electrode, which is attributed to the growth of Li<sub>2</sub>O<sub>2</sub> particles inside the paper electrode.<sup>17</sup> In this regard, the macropores were introduced to CNT and CNT/Mo<sub>2</sub>CT<sub>x</sub> electrodes to accommodate the discharge products. After PS removal, both electrodes showed highly porous structure with an average pore size of 2 μm, and the well-connected conductive networks were still maintained through the whole electrodes.

To verify the surface functionality of CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode, X-ray photoelectron spectroscopy (XPS) measurements were conducted and the results are shown in Fig. 2c–e. The Mo 3d spectrum is composed of Mo–C, Mo<sup>4+</sup>, and Mo<sup>6+</sup>. The binding energy at 227.95 eV and 232 eV are assigned to the Mo–C (3d<sub>5/2</sub>)

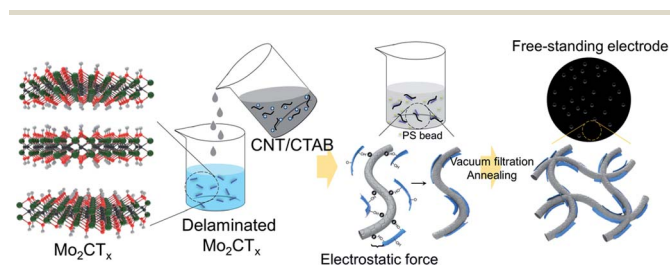


Fig. 1 Schematic of the CNT/Mo<sub>2</sub>CT<sub>x</sub> composite paper preparation.

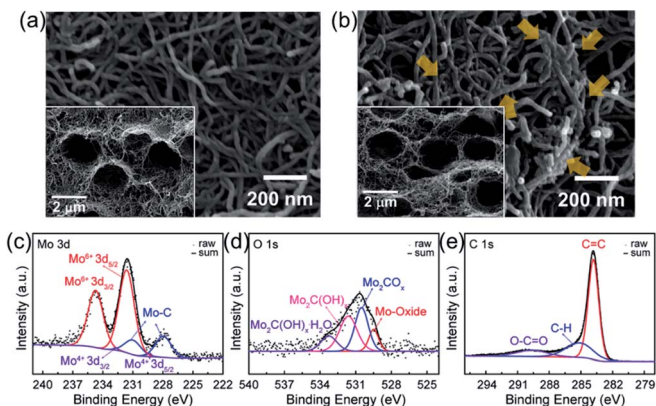


Fig. 2 SEM images of (a) CNT (top-view), (b) CNT/Mo<sub>2</sub>CT<sub>x</sub> (top-view) electrodes. Inset images for cross-sectional view. CNT/Mo<sub>2</sub>CT<sub>x</sub> (c) Mo 3d, (d) O 1s, and (e) C 1s spectra.

and Mo–C (3d<sub>2/3</sub>) species from CNT/Mo<sub>2</sub>CT<sub>x</sub>.<sup>10</sup> The O 1s spectrum is composed of species corresponding to the Mo-oxide, Mo<sub>2</sub>CO<sub>x</sub>, Mo<sub>2</sub>C(OH)<sub>x</sub>, and Mo<sub>2</sub>C(OH)<sub>x</sub>–H<sub>2</sub>O. The binding energy at 529.48 eV is assigned to the Mo-oxide, which is generated by surface oxidation.<sup>10</sup> The peaks at 530.5 and 531.62 eV are assigned to the –O terminated Mo<sub>2</sub>CO<sub>x</sub> and –OH terminated Mo<sub>2</sub>C(OH)<sub>x</sub>. The relatively small peak at 533.25 eV is assigned to Mo<sub>2</sub>C(OH)<sub>x</sub>–H<sub>2</sub>O.<sup>10</sup> The C 1s spectrum is composed of components corresponding to the C=C, C–H, and O–C=O at the binding energy of 283.81, 285.13 and 289.61 eV, respectively.<sup>14</sup> Hence, the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode contains abundant functional groups including -oxide, -O<sub>x</sub>, -(OH)<sub>x</sub>, and -(OH)<sub>x</sub>–H<sub>2</sub>O.

To investigate the effect of the Mo<sub>2</sub>CT<sub>x</sub> catalyst, the electrochemical performance of the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was evaluated and compared with the CNT electrode. The as-prepared paper type electrodes were assembled into the Li–O<sub>2</sub> cell and tested with constant current under limited capacity and limited voltage conditions. When the Li–O<sub>2</sub> cell was discharge with the CNT electrode at 100 mA g<sub>CNT</sub><sup>–1</sup> in a 2.0 V cut-off condition, the capacity was 5950 mA h g<sub>CNT</sub><sup>–1</sup> (Fig. 3a). The discharge capacity

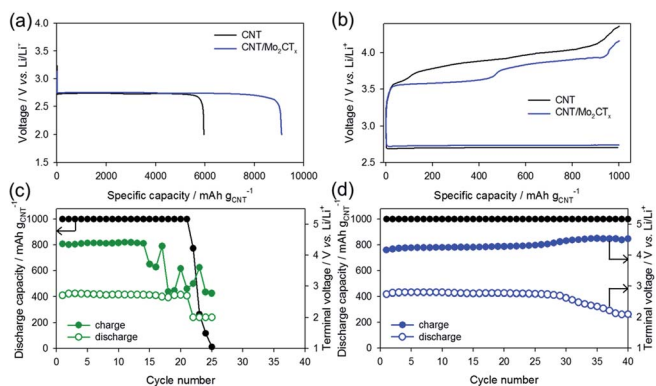


Fig. 3 (a) Discharge capacity and (b) voltage profiles of CNT and CNT/Mo<sub>2</sub>CT<sub>x</sub> electrodes, cycle life of (c) CNT electrode and (d) CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode.

of the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was 9100 mA h g<sub>CNT</sub><sup>-1</sup>, which is much higher than that of the CNT electrode. Because the surface area of the cathode is related to the discharge capacity, it is necessary to examine the surface area of the CNT and CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode. The BET measurements were conducted on both electrodes and the results are presented in Table S1.† Although the surface area of the CNT/Mo<sub>2</sub>CT<sub>x</sub> is smaller than that of the CNT, the CNT/Mo<sub>2</sub>CT<sub>x</sub> showed much higher discharge capacity. Thus, the Mo<sub>2</sub>CT<sub>x</sub> introduction greatly improves discharge capacity by promoting the Li<sub>2</sub>O<sub>2</sub> formation.

On the other hand, Li–O<sub>2</sub> cells were cycled in a limited capacity of 1000 mA h g<sub>CNT</sub><sup>-1</sup> with a current density of 200 mA g<sub>CNT</sub><sup>-1</sup>. The voltage profiles of the 1<sup>st</sup> cycle were shown in Fig. 3b that the OER overpotential was reduced by the Mo<sub>2</sub>CT<sub>x</sub> introduction to the electrode. Moreover, the CNT/Mo<sub>2</sub>CT<sub>x</sub> exhibited better cycling performance over 40 cycles than that of the CNT electrode (Fig. 3c and d). In this regard, the catalytic activity of Mo<sub>2</sub>CT<sub>x</sub> toward Li–O<sub>2</sub> reactions were demonstrated and the Mo<sub>2</sub>CT<sub>x</sub> MXene can be considered as an effective catalyst for Li–O<sub>2</sub> batteries.

In order to verify the Li<sub>2</sub>O<sub>2</sub> formation pathway of the Mo<sub>2</sub>CT<sub>x</sub> incorporated cathode, the *ex situ* XRD and SEM were carried out. The CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was discharged until the voltage reaches at 2.0 V with constant current of 100 mA g<sub>CNT</sub><sup>-1</sup>, and then the cell was disassembled to analyse the discharge product.

The *ex situ* XRD pattern in Fig. 4a exhibited that 2 theta values at 32.89, 34.97 and 58.72 degrees correspond to the (1 0 0), (1 0 1) and (1 1 0) planes were assigned to the typical Li<sub>2</sub>O<sub>2</sub> (JCPDS#01-074-0115). Thus, the discharge product was demonstrated as Li<sub>2</sub>O<sub>2</sub>, the main product of Li–O<sub>2</sub> reactions, which signifies that the prepared electrode obeys the fundamental principles of Li–O<sub>2</sub> batteries.

The SEM image of the discharge product (Li<sub>2</sub>O<sub>2</sub>) shows that the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was almost covered with typical

toroidal Li<sub>2</sub>O<sub>2</sub> with a particle size of 1 μm (Fig. 4b). To clarify the effect of Mo<sub>2</sub>CT<sub>x</sub> on the toroidal Li<sub>2</sub>O<sub>2</sub> formation, the CNT electrode was disassembled after discharge, then the SEM images were taken (Fig. S2†). Unlike the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode, the surface of the discharged CNT electrode was covered with thick deposits and sparse distribution of toroidal Li<sub>2</sub>O<sub>2</sub>. Thus, it is clear that this highly covered toroidal morphology is originated from the high surface coverage of MXene. The fully covered surface functional groups inhibit the access of O<sub>2</sub> on the surface of Mo<sub>2</sub>C, preventing the adsorption of O<sub>2</sub> on Mo. Consequently, this inaccessibility of O<sub>2</sub> to the cathode surface hinders the nucleation of the intermediate (LiO<sub>2</sub>) on the cathode surface, which derives the solution growth model to undergo Li<sub>2</sub>O<sub>2</sub> nucleation in the electrolyte, resulting in toroidal morphology.<sup>3</sup> The schematic representation of the Li<sub>2</sub>O<sub>2</sub> nucleation process with CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was illustrated in Fig. 4c.

It is noteworthy that non-functionalized molybdenum carbide (Mo<sub>2</sub>C without functional groups) has been previously reported to generate the thin film type Li<sub>2</sub>O<sub>2</sub>, which suggests the surface growth model for Li<sub>2</sub>O<sub>2</sub> nucleation. The origin of this formation mechanism is supposed to be the lack of coordination vacancy of Mo, which leads to a strong affinity between O<sub>2</sub> and Mo<sub>2</sub>C, resulting in the surface growth model of Li<sub>2</sub>O<sub>2</sub>. Kwak *et al.* reported the Mo<sub>2</sub>C/carbon nanotube composite with excellent Li–O<sub>2</sub> battery performances, operated under 1 M LiCF<sub>5</sub>O<sub>3</sub> in TEGDME at 100 mA g<sup>-1</sup>, attributed to the formation of MoO<sub>3</sub>-like layers on the Mo<sub>2</sub>C nanoparticles by chemisorption of O<sub>2</sub> on the surface of Mo.<sup>15</sup> The morphology of Li<sub>2</sub>O<sub>2</sub> after discharge was confirmed as a well dispersed thin layer type. Zhu *et al.* developed carbon-wrapped Mo<sub>2</sub>C nanoparticles and CNTs on Ni foam as a cathode, operated under 1 M LiTFSI in TEGDME at 200 mA g<sup>-1</sup>, and the discharge product was uniformly coated on the surface of the CNTs.<sup>16</sup> Since we used 1 M LiNO<sub>3</sub> in DMAC as electrolyte, which is known as a strong solution growth facilitator, it is necessary to eliminate the electrolyte effect to clarify the role of Mo<sub>2</sub>CT<sub>x</sub>. In this regard, the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was discharged at 100 mA g<sup>-1</sup> in a 2.0 V cut-off condition under 1 M LiTFSI in TEGDME, which has low donor number, and the resultant discharge product was observed by SEM. As shown in Fig. S3b,† the surface of CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode was covered by discharge product with nearly spherical-like morphology without any thin film formation. These results imply that the Mo<sub>2</sub>C catalyst-mediated Li<sub>2</sub>O<sub>2</sub> nucleation is governed by the surface growth model.

To understand the effect of the surface functional groups on the Li<sub>2</sub>O<sub>2</sub> formation pathway, density functional theory (DFT) with PBE-D3 method. The hydroxyl group (–OH) was selected as the functional group because it is the least stable species so can desorb first.<sup>9</sup> For the OH-terminated MXene (Mo<sub>2</sub>C(OH)<sub>2</sub>) in shown as Fig. 5a, there are three representative possible configurations (model 1: OH groups are located on the top of Mo metal; model 2: OH groups are located on the top of carbon in Mo<sub>2</sub>C(OH)<sub>2</sub> single layer at the hollow sites; model 3: OH groups are located on the another hollow site which is position of Mo in bottom of Mo<sub>2</sub>C(OH)<sub>2</sub> single layer). In order to calculate the O<sub>2</sub> adsorption on the surface of Mo<sub>2</sub>C(OH)<sub>2</sub>, the most stable model 3 of Mo<sub>2</sub>C(OH)<sub>2</sub> was selected by the vibrational

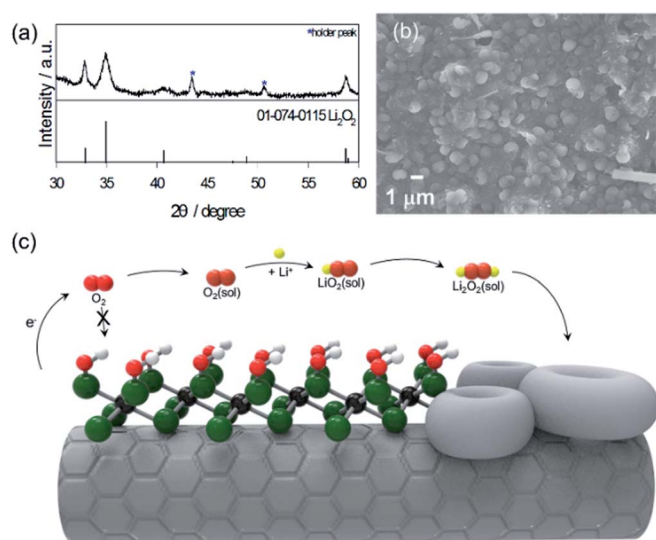
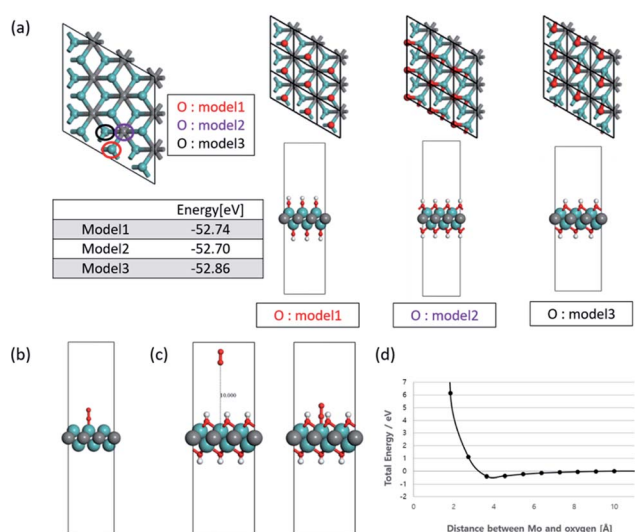


Fig. 4 (a) *Ex situ* XRD, (b) SEM image of CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode after discharge, (c) schematic of the Li<sub>2</sub>O<sub>2</sub> formation for the CNT/Mo<sub>2</sub>CT<sub>x</sub> electrode.



**Fig. 5** (a) Representative three configurations of  $\text{Mo}_2\text{C}(\text{OH})_2$  and their total energy. The colored circles are location of oxygen atom in hydroxide. The hydrogen atom in hydroxide is omitted in the figures for convenience, (b) the optimized configuration for  $\text{O}_2$  adsorption on  $\text{Mo}_2\text{C}(\text{OH})_2$  surface, (c) the configurations for  $\text{O}_2$  adsorption on the surface of model 3 of  $\text{Mo}_2\text{C}(\text{OH})_2$ , and (d) the fixed single-point energies in accordance with distances between the top of Mo metal from model 3 and the oxygen molecule.

frequency analysis and the energy of the geometry optimized structures when absorbing  $\text{O}_2$ . The vibrational frequency analysis indicates that  $\text{Mo}_2\text{C}(\text{OH})_2$  have some imaginary frequencies, on the other hand,  $\text{Mo}_2\text{C}$  have a no imaginary frequency in Fig. S4.† These tendencies are also found in  $\alpha\text{-Mo}_2\text{C}^{24}$  as well as  $\beta\text{-Mo}_2\text{C}$ . Although  $\text{Mo}_2\text{C}(\text{OH})_2$  have dynamic instability from the analysis of phonon dispersion, model 3 is regarded as at least the most stable structure because model 3 have the lowest geometry optimized energy ( $-52.86$  eV) and only one small imaginary frequency when comparing model 1 and 2 (each  $-52.74$  and  $52.70$  eV).

As such, the OH-terminated MXene for model 3 was selected as the configuration to examine the binding energy of  $\text{O}_2$ . The  $3 \times 3$  slabs of  $\text{Mo}_2\text{C}$  and  $\text{Mo}_2\text{C}(\text{OH})_2$  were utilized for the adsorption energy of  $\text{O}_2$ . At first, non-terminated  $\text{Mo}_2\text{C}$  surface was computed to be  $-272$  kJ mol $^{-1}$  (Fig. 5b), while that of  $\text{Mo}_2\text{C}(\text{OH})_2$  led to non-convergent result. As such, the position of all the atoms were fixed in the simulations to obtain the fixed single-point energies for varying  $\text{O}_2$  positions relative to the  $\text{Mo}_2\text{C}(\text{OH})_2$  surface (Fig. 5c). Specifically the  $\text{O}_2$  molecule was initialized at a distance 10 Å from top of the Mo metal with subsequent configurations coming closer to the top of the Mo metal from model 3. The resulting single point energy data (Fig. 5d) reveals that  $\text{O}_2$  cannot bind to the surface of  $\text{Mo}_2\text{C}(\text{OH})_2$ , implying that  $\text{LiO}_2$  nucleation as well as  $\text{Li}_2\text{O}_2$  cannot possibly occur on the surface of  $\text{Mo}_2\text{CT}_x$  surface. This is consistent with the experimental finding and corroborates that the toroidal  $\text{Li}_2\text{O}_2$  formation pathway is resulted from the inaccessibility of  $\text{O}_2$  on the cathode surface.

## Conclusions

We found that MXene with abundant functional groups not only enhanced the battery performance but also played a significant role in determining the  $\text{Li}_2\text{O}_2$  formation pathway. The discharge capacity, overpotential and cycle life were improved by introducing  $\text{Mo}_2\text{CT}_x$  on CNTs, which manifest that the  $\text{Mo}_2\text{CT}_x$  exhibits good catalytic activity toward Li– $\text{O}_2$  reactions. The high surface coverage of  $\text{Mo}_2\text{CT}_x$  with functional groups resulted in the toroidal  $\text{Li}_2\text{O}_2$  formation *via* the solution growth model. This is attributed to the inaccessibility of  $\text{O}_2$  to the cathode surface, which was verified by the DFT calculations.

It is noticeable that here we only studied one type of MXene, but more diverse MXenes can play a critical role in determining the  $\text{Li}_2\text{O}_2$  formation pathway due to their extraordinarily high surface coverage. We believe this study will provide guidelines for a large family of MXenes to be considered as effective catalysts for the Li– $\text{O}_2$  batteries in the future.

## Conflicts of interest

There are no conflicts to declare.

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