Unveiling the reaction selectivity mechanism of molybdenum and tungsten carbides as cathode catalysts for Li-CO₂ batteries

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1. Supplementary Methods

In this work, all calculations were performed using first principles calculations based on density functional theory (DFT), using the Vienna ab initio Simulation Package (VASP) software package. The interaction between valence electrons and ionic solids was described by the projected augmented wave (PAW) potential.^{S1} The Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) was used to describe the exchange correlation energy.^{S2-S4} The adsorption behavior of Li-CO₂ battery have weak interaction, which was corrected by zero damping DFT-D3 method of Grimme. The kinetic energy cutoff energy of 450 eV is adopted, and the convergence of electron energy is ensured. The gamma k-point grid was used to sample the first Brillouin region,^{S5} and a $2 \times 2 \times 1$ k-point was used for Mo₂C(101) with a size of 14.11×12.12 Å and $W_2C(101)$ with a size of 14.13×12.21 Å. The total energy and interatomic force converge to 1.0×10^{-5} eV and 0.01 eV A⁻¹, respectively. Mo₂C(101) and W₂C(101) consisting of three molecular layers were constructed and the lower one molecular layer was fixed to simulate the infinite extension of the bulk structure. In addition, a vacuum layer of 20 Å was applied in a direction perpendicular to the surface to simulate isolated upper and lower surfaces.

The thermodynamic properties of carbonates and oxalates on the pristine or covered Mo₂C(101) (W₂C(101)) were investigated by calculating the Gibbs free energy (*G*) of the intermediates during the reaction. Using the previously reported computational model,^{S6, S7} which employs the anode in a Li-CO₂ battery as a reference electrode, it allows us to replace the chemical potential (μ) of the Li⁺+e⁻

pair with that of a Li atom in the lithium metal bulk. It can also be expressed as the equilibrium potential for the reaction $\text{Li}^++e^- = \text{Li}$ is 0 V. For each step of the reaction, the Gibbs free energy change (ΔG) is the change in the free energy of the initial and final states and is expressed by the following formula: $\Delta G = \Delta E_{\text{DFT}}$ $+ \Delta E_{\text{ZPE}} - T\Delta S - eU$, where ΔE_{DFT} , ΔE_{ZPE} , *T*, ΔS , and *U* are the electron energy difference, zero point energy difference, temperature (298.15 K), entropy difference and applied potential. The entropy is the contribution of the vibration mode to the entropy obtained by calculating the vibration frequency.

2. Supplementary figures



Figure S1. Atomic structure of (a) Mo_2C and (b) W_2C . Side and top views of (c) $Mo_2C(101)$ and (d) $W_2C(101)$. The dashed line separates the minimum periodic cell, and the supercell contains two periods in the directions of the two basis vectors parallel to the surfaces.



Figure S2. The detailed electrochemical pathways of the Li-CO₂ batteries reaction on Mo₂C(101). The orange (green) number represents ΔG at the equilibrium potential of the lithium oxalate (carbonate) reaction path.



Figure S3. The detailed electrochemical pathways of the Li-CO₂ batteries reaction on W₂C(101). The orange (green) number represents ΔG at the equilibrium potential of the lithium oxalate (carbonate) reaction path.



Figure S4. The atomic structures of (a) *Li, (b) *CO₂, (c) *C₂O₄, (d) *LiC₂O₄, (e) *Li₂C₂O₄, (f) *CO, (g) *LiCO₂, (h) *Li₂CO₂, (i) *C, (j) *CO₃, (k) *LiCO₃ and (l)

* Li_2CO_3 for pristine Mo₂C(101).



Figure S5. The atomic structures of (a) *Li, (b) *CO₂, (c) *C₂O₄, (d) *LiC₂O₄, (e)

*Li₂C₂O₄, (f) *CO, (g) *LiCO₂, (h) *Li₂CO₂, (i) *C, (j) *CO₃, (k) *LiCO₃ and (l) *Li₂CO₃ for pristine W₂C(101).



Figure S6. The Gibbs free energy of the reactions for the formation of (a) $Li_2C_2O_4$ and (b) Li_2CO_3 at equilibrium potential on pristine $Mo_2C(101)$ and pristine $W_2C(101)$.



Figure S7. The crystal orbital Hamiltonian population (COHP) of C=C in $*C_2O_4$ adsorbed on the (a) pristine Mo₂C(101) and (b) pristine W₂C(101).



Figure S8. The density of states (DOS) of C-*p* and O-*p* in $*CO_3$ adsorbed on the (a) pristine and (c) covered Mo₂C(101). The COHP of C-O in $*CO_3$ adsorbed on the on the (b) pristine and (d) covered Mo₂C(101).



Figure S9. The DOS of C-*p* and O-*p* in $*CO_3$ adsorbed on the (a) pristine and (c) covered $W_2C(101)$. The COHP of C-O in $*CO_3$ adsorbed on the on the (b) pristine and (d) covered $W_2C(101)$.



Figure S10. The atomic structures of pristine surfaces with (a, b) one, (c, d) four, (e, f) five and (g, h) eight adsorbed CO_2 molecules for $Mo_2C(101)$ and $W_2C(101)$.

Both Mo₂C(101) and W₂C(101) contain two periods in the directions of the two basis vectors parallel to the surfaces(**Figure S1c and d**), and their structures covered by a molecular layer of CO₂ were investigated. The stable adsorption sites of individual CO₂ molecule on the pristine surfaces were investigated, as shown in **Table S1**. The results show that the adsorption configuration of site 1 has the lowest energy, as shown in **Figure S10(a) and (b**). On a surface covering four CO₂ molecules, CO₂ occupies all the most stable sites(Mo1 and W1 sites) within the supercell. For further adsorption of CO₂ molecules, two configurations were considered and shown in **Table S2**. The adsorption configuration at site 1(Mo2 or W2 sites) is thermodynamically more advantageous. When the substable sites(Mo2 or W2 sites) were fully covered, there were 8 CO₂ molecules on both supercells. The adsorption of the next CO₂ molecule will result in the dimerization of CO₂ molecules and the loss of the pristine CO₂ molecular configuration, as shown in **Figure 7 (g, h)**.



Figure S11. The atomic structures of (a) LiC_2O_4 , (b) $Li_2C_2O_4$, (c) $LiCO_3$ and

(d) $*Li_2CO_3$ for covered Mo₂C(101).



Figure S12. The atomic structures of (a) $*LiC_2O_4$, (b) $*Li_2C_2O_4$, (c) $*LiCO_3$ and (d) $*Li_2CO_3$ for covered W₂C(101).



Figure S13. Gibbs free energy of Li-CO₂ battery reaction at equilibrium potential on (a, c) $Mo_2C(101)$ and (b, d) $W_2C(101)$ covered by 1 ML of CO₂.



Figure S14. The DOS of the (a, c) s, p and (b, d) d orbitals of Mo1 and Mo2 in Figure S1(c). The DOS of the (e) s, p and (f) d orbitals of Mo1 in Figure S10(a).



Figure S15. The DOS of the (a, c) *s*, *p* and (b, d) *d* orbitals of Mo₁ and Mo₂ in Figure S10(g).



Figure S16. The DOS of the (a, c) s, p and (b, d) d orbitals of W1 and W2 in Figure S1(d). The DOS of the (e) s, p and (f) d orbitals of W1 in Figure S10(b).



Figure S17. The DOS of the (a, c) s, p and (b, d) d orbitals of W1 and W2 in Figure S10(h).



Figure S18. Electron locational fuction (ELF) of $*CO_2$ on (a) Mo₂C(101) and (b) $W_2C(101)$ covered by a molecular layer of CO_2 .



Figure S19. Bader charges of $CO_3+CO_3+CO_3$ adsorbed on (a) covered Mo₂C(101) and (b) covered W₂C(101).

3. Supplementary tables

Table S1. The structures of CO_2 at different adsorption sites on the pristine $Mo_2C(101)$ and $W_2C(101)$.

Pristine Mo ₂ C(101)				
Site 1	Site 2	Site 3		
Site 4	Site 5	Site 6		
Pristine $W_2C(101)$				
Site 1	Site 2	Site 3		
Site 4	Site 5	Site 6		

Table S2. The structures of 5 CO_2 molecules adsorbed on $Mo_2C(101)$ and $W_2C(101)$.

Mo ₂ C(101)		W ₂ C(101)		
Site 1	Site 2	Site 1	Site 2	

Notes and References

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