COMPUTATIONAL DETAILS AND FIGURES

All calculation in this work were carried out by first-principle calculation based on the periodic density functional theory (DFT), as implemented in CASTEP code[1,2]. The interactions between the ions and valence electrons were described by the Vanderbilt ultrasoft pseudopotential[3], using the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE)[4]. The atomic configurations of Ti, C, O and Li generated from the ultrasoft pseudopotential were $3s^2 3p^6 3d^2 4s^2$, $2s^2 2p^2$, $2s^2 2p^4$ and $1s^2 2s^1$, respectively.

The Broyden-Fletcher-Goldfarb-Shannon (BFGS)[5] algorithm was adopted to minimize the total energy of whole models and relax their structure to the ground state. For geometry optimization, the final convergent values for self-consistence are set at 2.0×10^{-5}eV/atom for total energy, 0.05eV/Å for force, 0.1GPa for maximum stress, and 0.002Å for the maximum displacement, respectively.

A kinetic energy cut-off value of 385eV was used in all models which contain TiC, including bulk model, surface slab models, Li_2O_2 cluster adsorption models, and Li_2O_2/TiC interface models. A cutoff energy of plane wave basis was set to 405eV for calculating the properties of Li_2O_2 crystal and its surface. And all of cutoff energy we applied was already tested on convergence.

The k-point meshes were set at 11×11×11 for the TiC bulk unit cell, and 11×11×1 for its surface slabs using Monkhorst-Pack scheme[6], which was utilized in all calculation. A 12Å vacuum is employed on both surface for TiC surface slabs, which was sufficient to ensure vanishing wave function overlap across the vacuum region. A 7×7×7 k-point mesh was set for the Li_2O_2 bulk unit cell, and 7×7×1 for its surface slabs, including a ~10Å vacuum region on both sides, which was test to be convergent. For calculating the adsorption of Li_2O_2 clusters, slab with 9Å vacuum region, and 3×3×1 k-point mesh was employed in 2×2 TiC(111) supercells. Note that the same mesh size was employed by Zhang et al.[7] for their study O_2 adsorption on TiC surface. For optimizing the geometry of the interface between Li_2O_2 and TiC surface, a thicker vacuum 14 Å and larger k-point mesh 7×7×1 were employed in

2×2 Li_2O_2(0001)/Ti(111) supercell. To avoid polarization effect, Li_2O_2 coating was applied to both sides of a nine atomic layer symmetric TiC slab.

To correct well-known O_2 overbinding problem, we follow the method described by Hummelshoj et al.[8] We used the gas phase reaction $2H_2 + O_2 \rightarrow 2H_2O$, with the DFT calculated H_2 and H_2O energies and the experimental formation energy of water to establish the O_2 energy.

The Mulliken population analysis was used to reveal the nature of the chemical bonds at the interface. The average bond length $\bar{L}$ and the average overlap bond population $\bar{n}$ are defined as follows:

$$\bar{L}(A-B) = \frac{\sum L_i N_i}{\sum N_i} \tag{4a}$$

$$\bar{n}(A-B) = \frac{\sum n_i N_i}{\sum N_i} \tag{4b}$$

$$N_i = \sum_j n(A_i - B_j) \tag{4c}$$

where L_i and n_i are the bond length and overlap bond population between atom A_i and atom B_j, respectively. N_i is the total overlap bond population of A_i contributed from all atom B_j.

The adsorption energies (E_{ad}) were calculated using the following formula:

$$E_{ad} = (E_{sub\text{-}ad} - E_{sub} - E_{mol})/N_{mol}$$

where $E_{sub\text{-}ad}$, E_{sub} and E_{mol} are the total energy of relaxed adsorption model, TiC substrate slab and Li_2O_2 cluster, respectively. N_{mol} represents the number of adsorbed Li_2O_2 clusters.

The surface energies (γ) were calculated using the following equation:

$$\gamma = \frac{1}{2A}(E_{slab} - N_A\mu_A - N_B\mu_B) \tag{1a}$$

where E_{slab} is the total energy of slab and E_{bulk} is the total energy of bulk. N_A and N_B are the number of the atom A and the atom B in the slab, μ_A and μ_B correspond to their chemical potential, respectively. The fraction of 1/2 accounts for the two surfaces of the slab. A stands for the surface area.

The ideal work of adhesion W_{ad} is a rough approximation to the energy required to separate the coating from the substrate at the interface, which is defined as:

$$W_{ad} = \frac{\sum_i E_i - E_{TiC/Li_2O_2}}{\Omega} \quad (5)$$

where E_i is the total energy of slab i (i=TiC, Li_2O_2). $E_{TiC/Li2O2}$ is the total energy of the interface system. Ω is the interface area.

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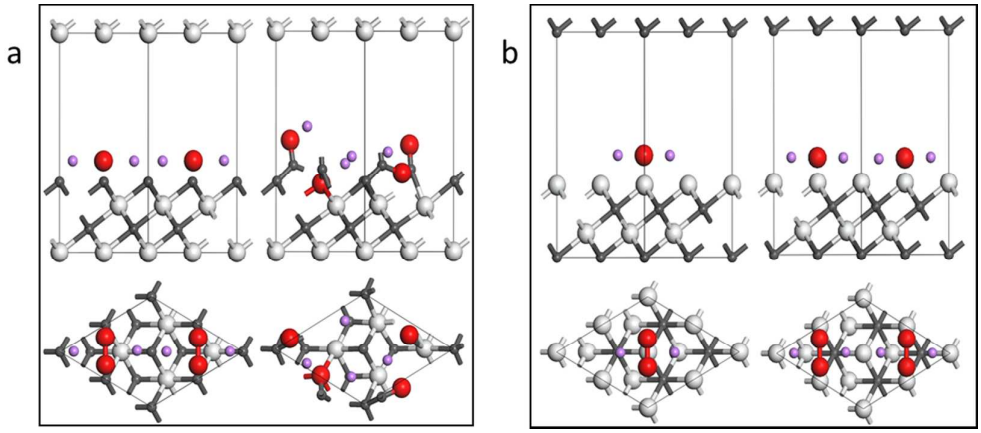

Figure s1. Side and top view of a) double Li_2O_2 adsorption on C-terminated TiC{111} surface, before (left) and after relaxation (right); b) single Li_2O_2 (left) and double Li_2O_2 (right) adsorption on Ti-terminated TiC{111} models before relaxation.

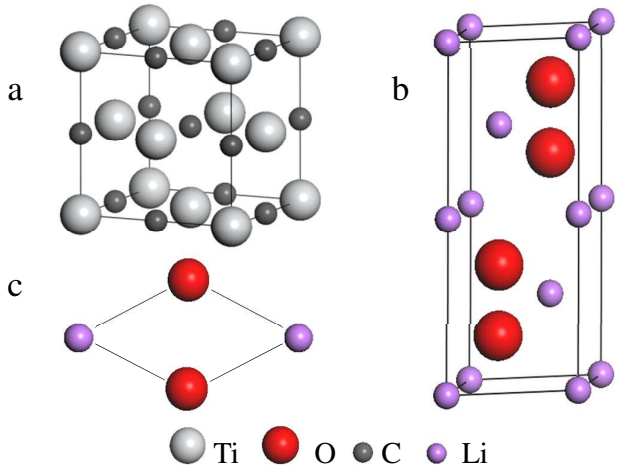

Figure s2. a) Cubic crystallographic structure of TiC, a = 4.329 Å, b) Hexagonal crystallographic structure of Li_2O_2, a = 3.177 Å, and c = 7.751 Å, c) Planar structure of Li_2O_2 cluster, O-O bond length = 1.56Å.

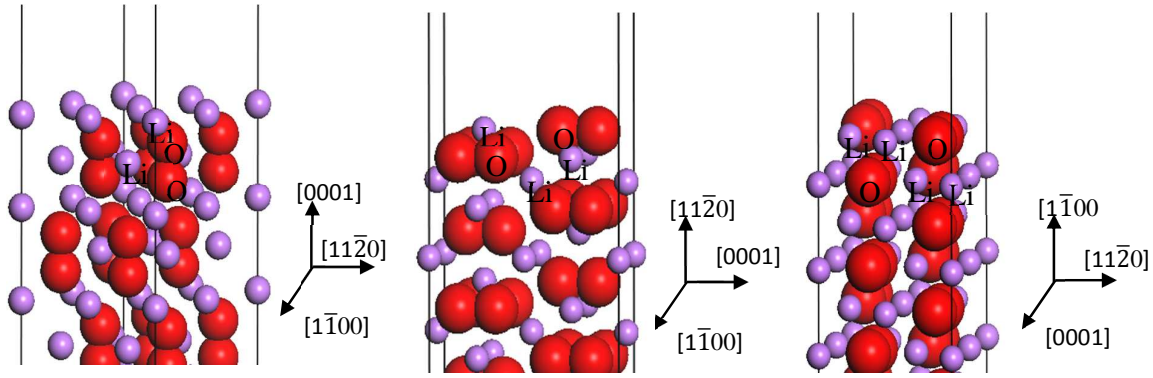

Figure s3. Labeling scheme for unique atom layer in the Li_2O_2 structure.

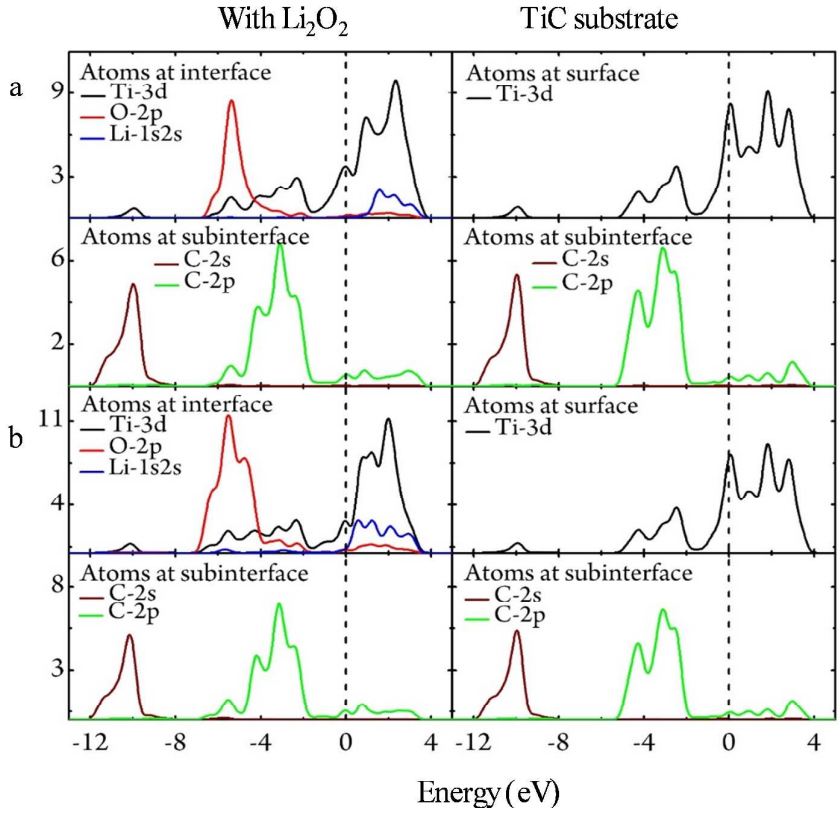

Figure s4. Angular momentum projected LDOS distribution for atoms at interface and sub-interface. a) One Li_2O_2 adsorption on Ti terminated Ti{111} surface, planar Li_2O_2 in parallel with TiC{111}, and b) Two Li_2O_2 adsorption on Ti terminated Ti{111} surface, planar Li2O2 in parallel with TiC{111}.