A First-Principles Study on CO Removing Mechanism on Pt Decorated Oxygen-rich Anode Surfaces (Pt_2/o-$MO_2(110)$, M = Ru and Ir) in DMFC

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Abstract:

Direct methanol fuel cell (DMFC) is an efficient power source. However, the DMFC anodes are easily toxified by CO or other hydrocarbons, which terminates the methanol oxidation reaction (MOR). The most commonly used high performance catalyst on DMFC anodes is Pt or bimetallic PtRu. In this work, we apply density-functional theory (DFT) to investigate the adsorption of CO and H_2O on pristine $Pt_2/MO_2(110)$ and the oxygen-rich Pt_2/o-$MO_2(110)$ surfaces (M = Ru and Ir). We find that the application of the oxygen-rich surfaces significantly reduces the adsorption energies of CO and H_2O molecules as well as the major reaction barrier ($CO + OH \rightarrow CO_2$) in the water-gas-shift-like (WGS-like) reactions forming CO_2. Our detailed analyses on the electronic interaction between the catalysts and adsorbates indicate that Pt_2/o-$MO_2(110)$ may be a promising DMFC anode material which reduces the poison problem, and that it may be the actual experimental system that is responsible for the observed efficient CO removal.

Keywords: Direct methanol fuel cell, CO removal, oxygen-rich surfaces.

Computational details

The density-functional theory (DFT) and the plane-wave method, as implemented in the Vienna ab initio simulation package (VASP), are employed to calculate the energies and structures of reactants, intermediates, transition structures and products of the reactions on $RuO_2(110)$ and $IrO_2(110)$. The projector-augmented-wave method (PAW) is used in conjunction with the generalized gradient-approximation (GGA) and Perdew−Wang 1991 (PW91) exchange-correlation functional, with a cutoff energy of 400 eV. The Monkhorst-Pack k-point grids are set as 4 x 2 x 1 and 4 x 6 x 1 for the (2 x 2) and (6 x 2)-$MO_2(110)$ (M = Ru and Ir) supercells, respectively. A vacuum space of over 12 Å is introduced to ensure negligible interactions between slabs. All layers are fully relaxed during optimization.

The adsorption energies are calculated based on: $E_{ads}=E_{(slab + adsorbate)}-(E_{slab} + E_{adsorbate})$, where $E_{(slab + adsorbate)}$, E_{slab}, and $E_{adsorbate}$ are the computed electronic energies of the surface with adsorbed molecule, the clean surface and the free molecule, respectively. The transition state structures are located by nudged-elastic-band (NEB) method, and the profiles of potential-energy surfaces (PES) are constructed accordingly. Frequency calculations are applied to verify the adsorbed intermediates and the transition states (with only one imaginary frequency).

Conclusions

Our DFT investigation shows that the o-rich surfaces (o-$MO_2(110)$) facilitate Pt dispersion more effectively than pristine surfaces. The calculation results indicate that the experimentally observed Pt dispersion may have occurred on the Pt_2/o-$MO_2(110)$ surfaces rather than the pristine $MO_2(110)$, as previously assumed. The Pt decorated oxygen-rich surfaces (Pt_2/o-$MO_2(110)$) significantly decrease the CO adsorption energies by about 0.8 eV than pristine $MO_2(110)$ surfaces, via the participation of the O_{cus} sites on o-$MO_2(110)$. Furthermore, the activation energy barriers of WGS reactions are significantly reduced on Pt_2/o-$MO_2(110)$. In summary, we believe that the formation of the o-rich surfaces is partially responsible for the observed high performance in catalytic reactions of DMFC anodes.

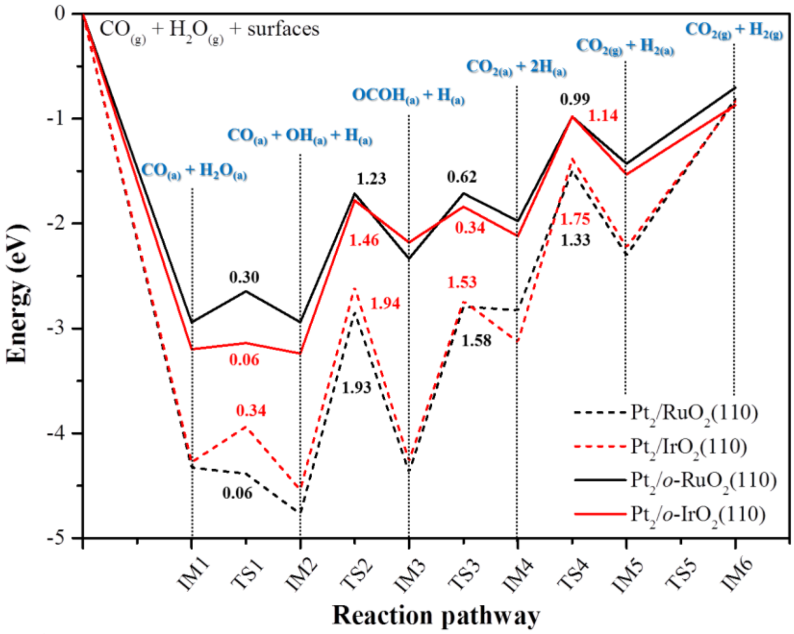

Figure 1. Calculated potential energy surface (PES) diagram for the WGS reaction on $Pt_2/RuO_2(110)$, $Pt_2/IrO_2(110)$, $Pt_2/o\text{-}RuO_2(110)$ and $Pt_2/o\text{-}IrO_2(110)$ surfaces. The intermediates (IMn, n=1-6) and the reaction barriers (in eV) for the transition states (TSn, n=1-5) for each reaction step are marked.

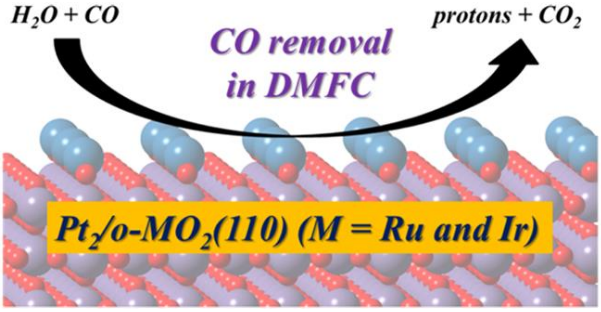

Figure 2. The CO removal reaction catalyzed by $Pt_2/o\text{-}MO_2(110)$ (M = Ru and Ir).

References

1. Liu, C.-Y.; Chang, C.-C.; Ho, J.-J.; Li, E. Y. *J. Phys. Chem. C* **2017**, *121*, 9825−9832.