

Quantum Chemical Analysis on Cermet Anodes for
Solid Oxide Fuel Cells

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INTRODUCTION

Toward the practical applications of solid oxide fuel cell (SOFC) technologies for either portable or stationary applications, research and development of anode materials are still important in order to directly utilize hydrocarbon fuels as well as to further improve the electricity conversion efficiency, the output power density, and the cost performance of the fuel cell systems. For the SOFC cermet anode, Ni/CeO₂ are well known to show high anodic activities for hydrogen fuel compared with Ni/ZrO₂. On the other hand, Cu/CeO₂ is reported to have sufficiently good anodic activities even for direct oxidation of hydrocarbon fuels. It is important to understand the roles of metal and oxide materials in cermet anode for the anodic activity, in order to design further active anode materials. However, the direct experimental analysis of SOFC anodic reaction is generally difficult because of its high operation temperature. On the other hand, dramatic increase of computational power and simulation theories make the computational chemistry approach a powerful and an effective method that can offer an electronic and atomistic information, which cannot be easily obtained by experimental approaches. We have developed an accelerated quantum chemical molecular dynamics program, “Colors”, based on original tight-binding approximations. The “Colors” program realizes several thousands times faster calculation compared with the conventional first-principles molecular dynamics methods, and thus supports the quantum chemical molecular dynamics analyses of complex systems containing rare-earth elements, which were difficult to be investigated so far. In this study, we investigated the characteristics of SOFC cermet anode using “Colors” program on the electronic and the atomic levels, in order to design anode materials with higher electrocatalytic activities.

METHOD

To study the influence of cermet anode materials on the anodic activities, we modeled Me/CeO₂ cermet anode (Me=Ni, Cu) as shown in Fig. 1. In the model, metal cluster that consists of 13 metal atoms is placed on CeO₂(111) surface and the calculations were carried out using “Colors” program.

RESULTS AND DISCUSSION

Table 1 summarizes the average charge of each element obtained from single point calculations by Colors program for the Ni/CeO₂ and Cu/CeO₂ cermet models shown in Fig. 1. The average charges for CeO₂ system are also shown for reference. The electron transfer from metal cluster to CeO₂ was observed for both Ni/CeO₂ and

Cu/CeO₂ systems and the metal cluster is positively charged as a result. Conversely, Ce and O atoms in CeO₂ are reduced, which would lead to the increase in electronic conductivity of CeO₂, thus can result in the higher catalytic activity of CeO₂ surface as electrode. Table 2 shows the partial density of states for both the highest occupied and the lowest unoccupied orbitals in each system. While in the CeO₂ system, both orbitals are mainly composed of O-2p, Ce-4f, and Ce-5d orbitals, the contribution from Ni orbitals becomes significant in Ni/CeO₂ cermet. On the other hand, the contribution from Cu orbitals is scarce in Cu/CeO₂ cermet and both the highest occupied and lowest unoccupied orbitals are mainly composed of O-2p, Ce-4f, and Ce-5d orbitals likewise CeO₂ system. The results indicate that 4s and 3d orbitals of Ni play an important role in the high catalytic activity of Ni/CeO₂ cermet for hydrogen fuel, and therefore the Ni/CeO₂ cermet might be easily deactivated due to the carbon deposition on Ni surface as experimentally known. On the other hand, the results also indicate that only O-2p, Ce-4f, and Ce-5d orbitals play an important role in Cu/CeO₂ system, which leads to the modest activity for hydrogen fuel and high tolerance

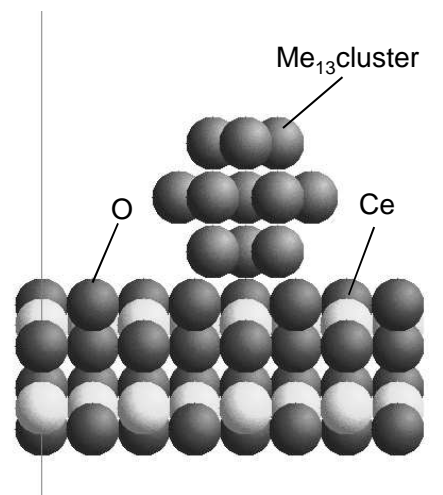


Fig. 1 Cermet anode model that consists of Me₁₃ cluster and CeO₂(111) surface (Me=Ni, Cu)

toward hydrocarbon fuels.

Table 1 Average charge of elements for Ni/CeO₂, Cu/CeO₂, and CeO₂ systems

| | Ce | O _{surface} | O _{inner} | Me |
|---------------------|-------|----------------------|--------------------|-------|
| Ni/CeO ₂ | +0.61 | -0.34 | -0.32 | +0.11 |
| Cu/CeO ₂ | +0.58 | -0.35 | -0.33 | +0.25 |
| CeO ₂ | +0.62 | -0.33 | -0.29 | - |

Table 2 Partial density of states for Ni/CeO₂, Cu/CeO₂, and CeO₂ systems

| | Energy level(eV) | Occp. No. | Density of States | Ce-6s | Ce-5d | Ce-4f | O-2p | Me-4s | Me-3d |
|---------------------|------------------|-----------|-------------------|-------|-------|-------|-------|-------|-------|
| | | | | | | | | | |
| Ni/CeO ₂ | -11.1 | 6 | 3 | 0.011 | 0.045 | 0.568 | 1.388 | 0.115 | 0.879 |
| | -11.05 | 0 | 4 | 0.056 | 0.143 | 0.573 | 2.126 | 0.865 | 0.367 |
| Cu/CeO ₂ | -10.85 | 3 | 2 | 0.002 | 0.127 | 0.408 | 1.445 | 0.005 | 0.000 |
| | -10.8 | 0 | 5 | 0.014 | 0.348 | 0.796 | 3.784 | 0.006 | 0.000 |
| CeO ₂ | -11.1 | 2 | 2 | 0.000 | 0.011 | 0.768 | 1.208 | - | - |
| | -11.02 | 0 | 2 | 0.000 | 0.141 | 0.486 | 1.356 | - | - |