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Developing a Thermal- and Coking-Resistant Cobalt–Tungsten Bimetallic Anode Catalyst for Solid Oxide Fuel Cells

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Supporting Information

ABSTRACT: We report the development of a novel Co−W bimetallic anode catalyst for solid oxide fuel cells (SOFCs) via a facile infiltration-annealing process. Using various microscopic and spectroscopic measurements, we find that the formed intermetallic nanoparticles are highly thermally stable up to 900 °C and show good coking resistance in methane. In particular, a fuel cell fitted with Co3W anode shows comparable activity (relative to Co) in the electro-oxidation of hydrogen and methane at 900 °C without suffering significant degradation during a longevity test.

KEYWORDS: nanoparticle, intermetallic compound, thermal stability, high temperature fuel cells, carbon resistance

In the global quest for efficient energy conversion, solid oxide fuel cells (SOFCs) are receiving more and more attention for decades, because of their higher fuel flexibility and efficiency.1−8 Indeed, their elevated operation temperature (600−800 °C) grants various advantages, such as improved electrokinetics and better overall thermal efficiency. However, this inevitably generates concerns regarding the thermal stability of the electrocatalyst, particularly when nanosized active species are used.9−15 In fact, metallic nanoelectrocatalysts are widely used as the anode component of SOFCs, offering improved fuel oxidation activity. Such well-dispersed nanoparticles expand the triple-phase boundary areas, demonstrate higher redox stability, and even resist coke formations.10,11,16 Unfortunately, these catalysts suffer from severe sintering problems, via either migration−coalescence or Ostwald ripening pathways.17 The inherent poor thermal stability remains a major challenge of their practical implementation.

Although organic capping agents, which are the commonly used stabilizers of nanoparticles, are not suitable for applications at temperatures of >400 °C,18−21 recent studies have shown promising alternative approaches for mitigating particle growth. These include (i) encapsulation of the catalytically active metal nanoparticle using a thin shell of oxides;22−25 (ii) the improvement of the metal−support interaction energy,16,26−30 e.g., via “socketing” nano species in the host oxides; and (iii) control of the three-dimensional (3-D) distribution of metal particles, achieving optimized interparticle spacings.31−33 However, the complex preparation protocols make these catalysts too costly for large-scale applications.

Another approach for increasing temperature stability is by preparing a bimetallic nanocatalyst34−38 that contains a higher-melting-point alloying element. This approach is restricted to specific chemical compositions, yet such alloys can enable the “best of two worlds”, combining superior activity with high stability, as well as improved price/performance ratios.39 In theory, this could open a route to active and stable fuel cell anodes. Specifically, the structurally ordered intermetallic compound has a well-defined composition and lattice structure, providing predictable control over various catalytic properties. Many of these catalysts have shown excellent electrochemical activity in fuel cell applications.40−44 Here, we report the synthesis of CoW bimetallic nanoparticle alloys and their application as SOFC anode catalysts. The optimized alloys exhibit exceptional thermal stability up to 900 °C, excellent electrochemical activity, and good coking resistance. We believe that this generic approach toward developing “self-stabilized” nanosized catalysts opens exciting opportunities for a variety of high-temperature catalytic processes.

We prepared catalyst samples with three compositions—Co, Co3W, and CoW—by infiltrating stoichiometric amounts of Co(NO3)2·6H2O and (NH4)10W12O41·5H2O onto the substrates, followed by calcination at 800 °C and annealing in hydrogen at 900 °C (see the Supporting Information for details). Figures 1a−e, as well as Figure S1, show the high-angle annular dark field (HAADF) image of 10 wt % Co3W on yttria-stabilized zirconia (YSZ) and the corresponding elemental mappings using energy-dispersive X-ray spectroscopy (EDX). Co and W formed bimetallic particles, yet no monometallic...
particles were identified. This shows the effectiveness of preparing alloys via this facile infiltration-annealing approach. The bimetallic nanoparticles, 10–50 nm in size, remained well-distributed over the YSZ, even after 24 h of annealing at 900 °C, implying an exceptional thermal stability for Co3W (see below). Examination of the high-resolution transmission electron microscopy (HRTEM) micrograph, as well as the diffraction pattern in Figure 1f, suggests that this nanoparticle had a Co3W intermetallic crystallographic phase, showing the (100) facet of Co3W. Morphological characterizations regarding CoW can be found in the Supporting Information (Figures S2 and S3). An additional core–shell structure, Co7W6@W, was identified on the YSZ surface. Their dispersion also demonstrated high homogeneity, with a typical dimension of ~30 nm.

X-ray diffraction (XRD) studies also offered evidence for the formation of the intermetallic phases. Looking at the XRD patterns in Figure 2a, we see that Co3W intermetallic compound (Joint Committee on Powder Diffraction Standards (JCPDS) File No. 65-3520) was produced in the Co3W sample, whereas a mixture of metallic W and intermetallic Co7W6 (JPCDS File No. 02-1091) formed in the CoW group. These observations were in good agreement with the TEM data and the prediction of the thermodynamic phase diagram.45 In these

Figure 1. (a) TEM-HAADF image of a Co3W bimetallic catalyst supported on YSZ and the corresponding EDX elemental mappings of (b) W (in red), (c) Co (in yellow), (d) Zr (in green), and (e) overlaid Co, W, and Zr for a single nanoparticle; (f) HRTEM micrograph of the Co3W nanoparticle shown in panel (e).

Figure 2. (a) XRD patterns of YSZ supported Co, Co3W, and CoW catalysts; the number shown in the bracket indicates the JPCDS file number. (b) Temperature-programmed reduction in hydrogen gas (H2-TPR) spectra of the catalyst precursors.
The precursor could be ascribed to the reduction of CoWO$_4$ that S$_4$ in the Supporting Information. The single peak of CoW species,$_{46}$ in the bimetallic precursor disappeared completely stretching mode of the W$_6$ intermetallic was maintained, with a power density drop of <10%. The high stability of the infiltrated LSCF cathode and the LST anode were reported elsewhere.$^{40,51}$ Thus, we maintain that the thermal stability of the metallic infiltrates is the key factor governing the long-term robustness of the specific cell (cf. the highly dispersive Co$\text{W}_6$ nanoparticles observed in Figure 1 after 24 h of annealing in H$_2$).

This conclusion was further supported by the Brunauer–Emmett–Teller (BET) specific surface area analysis and by scanning electron microscopy (SEM) of the heat-treated samples. Figure 3d compares the specific surface areas of four powder catalysts. The loading of the metallic species did increase the surface areas of YSZ, because of the presence of the impregnated nanoparticles. Relative to Co catalyst, this effect was much more prominent for bimetallic samples, suggesting
that smaller Co$_3$W and CoW infiltretes were sustained after the 24 h heat treatment. The SEM images in Figures 3e and 3f confirm the exceptional thermal stability of Co$_3$W. For clearer observations, the nanoparticles were infiltrated directly into the porous YSZ scaffold without preloading LST as the electronic conductor. After only 0.5 h of annealing at 900 °C in H$_2$, the Co nanoparticles coalesced substantially, forming big clusters ranging from 100 nm to 300 nm in size on the YSZ surface. This sintering effect of Co nanoparticles is well-documented.\textsuperscript{32,33} Conversely, the fine Co$_3$W nanostructure was not destructed by the heat treatment; the particle size remained <50 nm. Figure S8 in the Supporting Information shows a schematic comparison of the sintering resistances of these two nanoparticles.

Excitingly, the Co$_3$W catalyst also showed good coking resistance during a longevity test. Figure 4a shows the potentiostatic test under a constant voltage load of 0.7 V in a stream of methane. Only a trace of degradation was seen after more than 25 h. The corresponding polarization curves of the Co$_3$W cell in methane before and after this stability test are shown in Figure S9 in the Supporting Information (similarly, the comparison under OCV conditions was also shown). The slight degradation, particularly in the low potential region, might be mainly due to the sintering effect. Although methane decomposition is thermodynamically favorable at 900 °C, the carbon deposition in Co$_3$W cells was greatly suppressed, compared with the Co cell (see Figure S10 in the Supporting Information). Though carbon filament formation was observed that led to the decreased performances in Figure S9, the majority of Co$_3$W particles remained free of carbon deposits. Note that the Co cell degraded rapidly in methane, as a result of combined sintering and coking effects. In addition, the discharging test also compares the electrochemical stability of the Co and Co$_3$W cells in H$_2$, in which the Co$_3$W cell showed negligible degradation after the 24 h test. The semi-quantitative coking resistance measurement was performed using thermogravimetric analysis (TGA) before which the examined catalysts were subjected to a 5 h exposure to methane at 800 °C. Notably, the carbon deposits in Co/YSZ reached almost 7 wt % (see Figure 4b). This is not surprising, as cobalt nanoparticles are reported to be extremely active, catalyzing the methane conversion to carbon filaments/nanotubes.\textsuperscript{34,35} For both the Co$_3$W and the CoW bimetallic catalyst, the carbon contents were insignificant, demonstrating great potential for use in hydrocarbon fuels. The decoking mechanism might involve the formation of tungstic acid on the alloy surface (see Figure S3). This acid was reported to suppress carbon deposition in methane.\textsuperscript{96,97}

In conclusion, we have discovered that Co$_3$W nanoparticle alloys are excellent SOFC anode catalysts, with exceptional thermal stability and high activity. More generally, the facile “self-stabilizing” synthesis strategy reported here opens opportunities for the designing new catalysts for SOFCs and other high-temperature applications.

**ASSOCIATED CONTENT**

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b01197.

Experimental details and additional characterization data (TEM, XRD, FTIR, SEM, and electrochemical tests) (PDF)

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\section*{Notes}

The authors declare no competing financial interest.

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