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Electroless deposition of Co(Mn)/Pd-decorator into Y_2O_3-stabilized ZrO_2 scaffold as cathodes for solid oxide fuel cells

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ABSTRACT

In this work, we show that higher Co or Mn dopant content of up to 25 mol% on Pd can be obtained without modifying the original crystal structure of Pd *via* co-reduction synthesis route using hydrazine (N_2H_4), which is not achievable *via* conventional sol-gel route. The synthesized Co/Mn-doped Pd alloys can inhibit Pd agglomeration that hinders Pd use as an oxygen reduction reaction (ORR) promoter on solid oxide fuel cell (SOFC) cathode. The presence of Co or Mn on Pd lattice of Co/Mn-doped Pd alloy-decorated YSZ (Y_2O_3 stabilized ZrO_2) cathode provides dual advantages of improving the ORR performance of the cathode and enhancing the ORR performance stability during long term operation. Between 600 °C and 800 °C, $Pd_{0.90}Co_{0.10}O$-impregnated YSZ cathode displayed the highest ORR performance among PdO-, $Pd_{0.90}Co_{0.10}O$-, $Pd_{0.75}Co_{0.25}O$-, $Pd_{0.90}Mn_{0.10}O$-, and $Pd_{0.75}Mn_{0.25}O$-impregnated cathodes as indicated by its relatively low area specific resistance of 0.14 Ω cm^2 at 700 °C. Our thermal gravimetric analyses and scanning electron microscopy images revealed that the high electrochemical performance stability of Co/Mn-doped Pd alloys during 30 hour-cathodic current test correlates with their higher metal ↔ metal oxide conversion reversibility and microstructure stability under thermal cycling between room temperature and 900 °C (relative to Pd).

Introduction

Lowering the operating temperature of solid oxide fuel cells (SOFCs) can solve the problems related to high materials cost, the use of special seals and interconnects, long start-up time, and low system reliability [1]. The cathode component generally determines the overall performance of an intermediate temperature (500–700 °C) SOFCs (IT-SOFCs); thus highlighting the need for cathode with high electrocatalytic

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activity and structure stability [2,3]. One way to improve the cathode electrocatalytic activity at such intermediate temperature is the modification of the oxide-based cathode using noble metals [4–6]. For example, PdO impregnation to the porous SOFC cathode provided enhanced electrocatalytic activity as reflected by the significant reduction in the polarization resistance, relative to the non-Pd porous cathode, especially for the low frequency contribution that represents the oxygen adsorption and dissociation processes [7–11]. In the case of Pd + YSZ cathode (YSZ corresponds to 8 mol% yttria stabilized zirconia, a widely used electrolyte compound) in particular, the presence of electrocatalytically active nanosized Pd particles in the porous cathode enlarged the triple phase boundaries (TPBs, reaction contact areas between oxygen ions, electrons, and oxygen gases) [12–15]. The oxygen ions and electrons can access the TPBs *via* the continuous interpenetrating Pd-YSZ networks within such Pd-impregnated YSZ cathode [16]. The formation of small grain size is generally desirable in such composite porous cathode case to maximize the interfacial areas and TPBs between Pd and YSZ phases.

Despite its high electrocatalytic activity, Pd-impregnated cathodes typically show deteriorated electrochemical performance during long term operation due to Pd agglomeration and grain growth at high temperature (800 °C and above) and under cathodic current application [17,18]. Such agglomeration and grain growth can be minimized by alloying Pd with transition metals such as cobalt (Co), manganese (Mn), or zirconium (Zr), which essentially enhances the thermal stability of PdO and suppresses the re-oxidation behavior of Pd during the thermal cycling [19–22]. Extensive use of various transition metals in the field of electrocatalysis comes primarily from their high electrocatalytic activities [23–29]. Ai et al. evaluated the performance of $Pd_{0.95}M_{0.05}$ (M = Mn, Co, Ce, and Gd) infiltrated YSZ cathode for solid oxide electrolysis cells and reported that alloying with Co provided enhanced performance and stability [30]. While the original crystal structure was preserved, such alloying modified the original chemical and thermal behavior. We have recently reported that the impregnation of 5–10 mol% Co-doped Pd particles into the porous YSZ cathode manifested into enhanced electrochemical activity and improved long term stability with respect to the non-doped Pd-impregnated cathode [16].

Wet impregnation route, i.e., soaking the sintered porous cathode matrix with metal ions containing solution followed by calcination at 700–1000 °C in air, has been widely used to prepare single metal and binary metals modified oxide cathodes. Following such calcination, particularly in binary metals (i.e., Pd-doped) case, another metal such as Co or Mn can substitute Pd in the PdO lattice only in low dopant amount case, i.e., up to 10 mol% Co and 5 mol% Mn [16,22]. When the dopant amount was increased above such threshold, phase impurities formed, such as $PdCo_2$ and Co_3O_4 in 20 mol% Co-doped PdO case [16]. To increase the dopant amount in the PdO lattice beyond the normal threshold while keeping the original PdO structure, which is of interest to enhance the thermochemical stability of PdO nanoparticles even further, other advanced deposition routes need to be applied. For example, metals co-reduction sol-gel route deposition using hydrazine (N_2H_4) or methanol (CH_3OH) as the reducing agent can be performed to obtain more homogenous binary metals alloys with nanostructure within the porous cathode matrix [31]. Such process additionally enables the alloy formation at lower temperature relative to the conventional sol-gel process.

In this work, we prepared and characterized 10 and 25 mol% Co/Mn-doped Pd alloys, i.e., $Pd_{0.90}Co_{0.10}O$, $Pd_{0.75}Co_{0.25}O$, $Pd_{0.90}Mn_{0.10}O$, and $Pd_{0.75}Mn_{0.25}O$ *via* co-reduction sol-gel route using hydrazine (N_2H_4). Our results indicate that alloying with Mn or Co provide beneficial effect to the structure stability of PdO at high temperature. We then impregnated four different types of Co/Mn-doped Pd solutions into the porous YSZ cathodes and evaluated their resultant individual electrocatalytic performances for oxygen reduction reaction (ORR). We utilized higher Co or Mn dopant content that those reported in the previous works to assess the effect of such high dopant amount to the thermo chemical stability [16,22]. Up to 25 mol% Co or Mn can substitute Pd in PdO lattice when Co/Mn-doped Pd alloys were synthesized *via* our co-reduction route as evidenced by the retainment of the original PdO structure. 10 mol% Co-doped PdO-impregnated YSZ cathode displayed the highest electrochemical performance while 10 mol% Mn-doped PdO-impregnated YSZ cathode displayed the best stability during the 30 hour-symmetric cell test.

Experimental

10 and 25 mol% Co/Mn-doped Pd alloys, i.e., $Pd_{0.90}Co_{0.10}O$, $Pd_{0.75}Co_{0.25}O$, $Pd_{0.90}Mn_{0.10}O$, and $Pd_{0.75}Mn_{0.25}O$ were synthesized *via* metals co-reduction sol-gel route using N_2H_4. Note that these Co/Mn and Pd contents are theoretical target content for synthesis. In $Pd_{0.90}Co_{0.10}O$ case, for example, stoichiometric amounts of $PdCl_2$ (Analytic Reagent, Platinum Group Metals China) and $Co(NO_3)_2 \cdot 6H_2O$ (Analytic Reagent, Sinopharm Chemical Reagent Co. Ltd) with Pd:Co molar ratio of 90:10 were dissolved into de-ionized water under stirring. A required amount of 0.01 mol L^{-1} hydrazine (N_2H_4) solution was added into the solution mixture as the reducing agent to initiate Pd and Co reduction reaction during which a large number of particles crystallized out from the solution. These precipitates were then filtered out, washed repeatedly with de-ionized water, dried at 180 °C for 12 h, and calcined at 750 °C for 5 h in air inside a muffle furnace; giving the final $Pd_{0.90}Co_{0.10}O$ powder.

Nano-structured Co/Mn-doped Pd alloy-impregnated YSZ cathodes were prepared using porous YSZ-dense YSZ bi-layer substrate (i.e., electrode-electrolyte bi-layer structure substrate) by wet impregnation. YSZ electrolyte substrate was initially fabricated using 8 mol% Y_2O_3 in ZrO_2 (YSZ) powder (Tosoh, Japan) by dry pressing followed by sintering at 1400 °C for 5 h in air. The sintered YSZ substrates were mechanically polished. On top of this sintered substrate, an additional porous YSZ layer was subsequently deposited by screen printing of YSZ slurry and calcination at 1200 °C for 1 h in air. This layer formed a porous YSZ scaffold on top the dense YSZ electrolyte substrate. The porous layer was about 10–20 μm thick while the electrode area was about 0.5 cm^2. To make Pd

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