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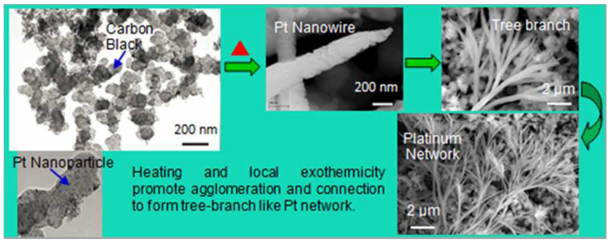
Graphic Abstract



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ARTICLE TYPE

A Platinum Nanowire Network as Highly Efficient Current Collector for Intermediate Temperature Solid Oxide Fuel Cells

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We report the fabrication and evaluation of a platinum nanowire network as highly efficient current collector for solid oxide fuel cells (SOFCs). The ink of carbon-black supported platinum nanoparticles was sprayed onto the cathode. After firing, the carbon black was oxidized and disappeared as carbon dioxide gas while the platinum nanoparticles connects with one another, forming tree-branch-like nanowire network. The diameters of the nanowires range from 100 nm to 400 nm. Compared to conventional platinum paste current collector, the polarization resistance of $PrBaCo_2O_{5+\delta}$ (PBCO) cathode with nanowire current collector was reduced by 44% at 650 °C (from 0.18 Ω cm^2 to 0.1 Ω cm^2). The peak power density of the button cells was improved at different degrees of 31.8%–59.6% under temperatures 650 °C–550 °C for typical cathode materials of PBCO, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). The nanowire network did not show obvious changes after long term test (400 h).

To improve the durability and reduce the cost of solid oxide fuel cells (SOFCs), significant efforts have been put into lowering the operating temperature of SOFCs to intermediate range of (400–600 °C).[1-7] However, the high ohmic resistance loss in the electrolyte and high polarization resistance loss in the cathode are two key obstacles toward the development of high performance intermediate temperature SOFCs.[8-10] The high ohmic resistance can be overcome through the development of thin film electrolyte built upon the anode-supported SOFC designs.[11-13] The high polarization resistance loss in the cathode can be reduced by developing high performance cathode materials. $La_{1-x}Sr_xMnO_3$ (LSM) has been widely used as the cathode material at early stages in the development of SOFCs.[14-16] Since the LSM is an electronic conductor, the composite cathodes formed by mixing the LSM with electrolyte materials such as yttria-stabilized zirconia (YSZ) then are developed to improve the ionic conductivity and oxygen reduction reaction (ORR) sites of the cathodes.[17] Later on, the mixed ionic and electronic conducting (MIEC) cathode materials such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)[18, 19] and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)[20] are developed so that the same material can conduct both electrons and ions simultaneously. As a result, the ORR sites can be extended to the entire surface of porous cathode. In recent years, the layered perovskites such as $PrBaCo_2O_{5+\delta}$ (PBCO) are investigated as the promising intermediate temperature cathode materials.[21-23] The high performance cathode may also be achieved with microstructure innovations via infiltration techniques.[24, 25]

Although many cathode materials mentioned above have been extensively studied, the conductivity of these materials is usually on the order of 10^2 S/cm, which is low in conducting electrons between the ORR sites and external circuit. To compensate for the low conductivities of cathode oxides, the current collector is typically employed in SOFCs.[26] Consequently the electrons needed by ORR can be transported from the external circuit to the reaction sites with minimum ohmic loss. Despite of the significant importance, the designs of current collectors do not receive too much attention in open literatures. Usually the platinum ink or platinum paste is simply painted on the cathode surface. After sintering, the organic substance is burn out while the platinum is attached to the cathode surface.[27] In order to reduce the polarization resistance, the cathode should have high conductivity and catalytic activity as well as be porous enough to allow oxygen readily to diffuse to the ORR sites.[28] If too much platinum is painted on the cathode surface, it might block the surface open pores, increasing the resistance of oxygen diffusion. Conversely the current collector with less platinum may avoid blocking the surface open pores of cathode porous structure; it can only connect less ORR sites to the external circuit. In this situation, the ORR sites, not directly connected to the current collector, have to conduct electrons through the cathode oxide. Accordingly the ohmic resistance increases. The ideal current collector should directly connect the ORR sites while leaving the open pores unblocked as much as it can. Obviously these two objectives are competing or conflicting with each other. It is difficult for traditional preparation methods of current collectors to achieve these two goals simultaneously.

Herein we report the fabrication and evaluation of a nano-scale current collector for intermediate temperature SOFC cathodes. A spray process is employed to coat the ink of carbon-black supported platinum nanoparticles on the cathode surface. After firing, the platinum nanowire-network is formed on the surface of the cathode, which can connect the ORR sites at the nano-scale to the external circuit while being able to substantially avoid blocking the open pores of the cathode. The experimental results have successfully demonstrated that such a platinum current collector is able to significantly reduce the cathode polarization resistance and improve SOFC performance. The stability of the current collector is also examined under large current discharge conditions for 400 hours. The developed method can be readily scaled up for mass productions.

The transmission electron microscopy (TEM) image of Fig. 1a shows that the platinum nanoparticles are uniformly coated on the surface of the carbon black. The thermo gravimetric analysis (TGA) shows a significant weight loss of the platinum coated carbon black powders between 330 °C and 550 °C (Fig. S1†), indicating that the carbon black was oxidized and became into carbon dioxide gas. The differential scanning calorimetry (DSC) indicates significant heat release because of carbon black oxidation. It is reasonable to believe that the platinum coated carbon black sprayed on the cathode should have the similar behavior during the heating up process in the furnace. The release of heat from the test furnace together with local exothermicity from the carbon black oxidation promoted the platinum nano-particles to agglomerate and connect with one another, forming the tree-branch-like nano-wire network as observed from field-emission scanning electron microscopy (FESEM) in Fig. 1b. The diameter of the nano-wires ranges from about 100 nm to 400 nm (Fig. 1c and 1d). Obviously such a nanowire network current collector is able to directly connect the ORR sites to the external circuit using its network branches. The magnified FESEM image (Fig. S2a†) shows that the platinum nano-network is composed of many small trees connected with one another through their branches. Meanwhile, the nano-network can effectively avoid blocking the surface open pores of the cathode. This can be seen from Fig. S2b†, where the large open pores on cathode surface were still present uniformly. The platinum nano-network even reached the internal surface of the open pores (Fig. S2c†). Therefore current collector with nano-wire network can achieve facile oxygen diffusion. By contrast, the current collector fabricated by painting the Pt paste shows a relatively thick layer covered on the cathode surface (Fig. S2d†), which could block the surface open pores of the cathode particularly the small open pores, significantly increasing the resistance of oxygen diffusion.

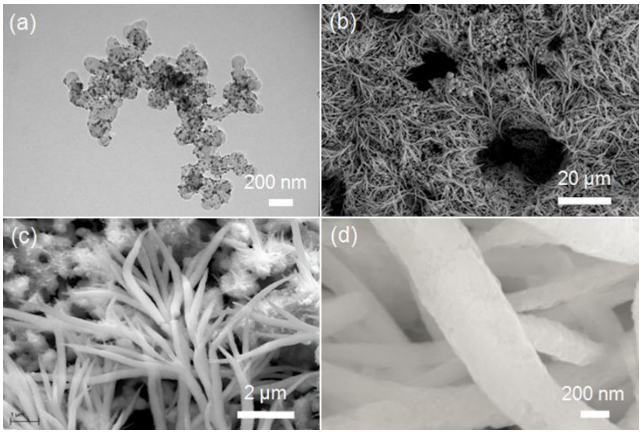

Fig. 1 (a) TEM image of carbon black supported platinumnanoparticles; (b) the FESEM image of cathode surface view with novel platinum nanowire network structured current collector; (c) Magnification of cathode surface with platinum nanowire network; (d) single platinum nanowire.

The performance of the platinum nanowire network as current collectors was evaluated by measuring the electrochemical impedance spectra (EIS) of the symmetric cells of PBCO/SDC electrolyte/PBCO, where the either side of the symmetrical cell was covered with the nanowire current collector. The Pt nanowire loading was controlled by the spraying/ejecting time length of the platinum nanoparticle coated carbon black ink. Here the spraying time of 20 seconds was used as an example. Fig. 2a shows EIS curves of the symmetrical cell measured in ambient air at 650 °C. The high-frequency intercept with the real-axis is primarily due to the electrolyte ohmic resistance (R_o) while the difference between the low frequency and high frequency intercept represents the overall electrode polarization resistance (R_p). From Fig. 2a, we can see that the R_p was only 0.1 Ω cm^2 with the nanowire network current collector. With the conventional Pt paste as the current collector, the R_p reached about 0.18 Ω cm^2. Therefore, it is reasonable to believe that the nanowire network current collector plays an important role in reducing the electrode polarization resistance. Accordingly the loading of platinum nanowire on the electrodes of the symmetric cells was varied by systematically changing the spraying time length of platinum coated carbon black ink. The corresponding polarization resistance (R_p) was measured using EIS technique in ambient air at 650 °C. As shown in Fig. 2b, with the spraying time length of 5 seconds, the R_p was as high as 0.37 Ω cm^2. Increasing the spraying time length to 10 seconds, the R_p was significantly reduced to 0.18 Ω cm^2. When the spraying time was increased to 15 seconds and 20 seconds, the R_p was reduced to 0.14 Ω cm^2 and 0.1 Ω cm^2 respectively. Further increasing the spraying time to 25 seconds and 30 seconds, however, the R_p was in turn increased to 0.22 Ω cm^2 and 0.32 Ω cm^2 respectively. The optimal spraying time is about 20 seconds.

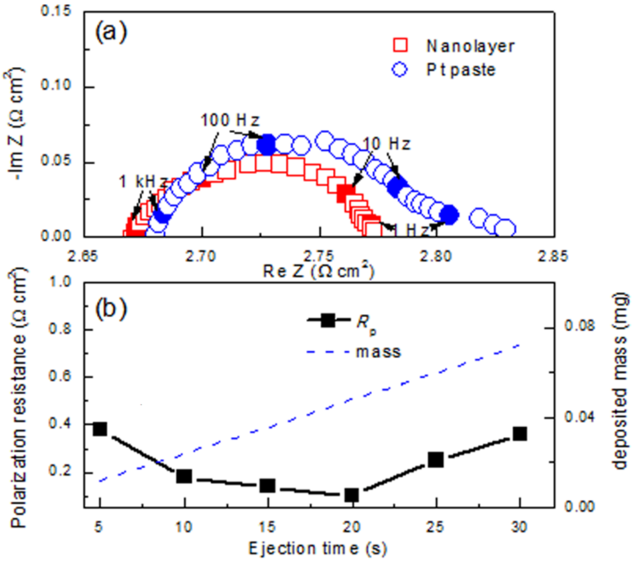

Fig. 2(a) The Nyquist plots of symmetric cells with composition of PBCO/SDC/PBCO with different types of current collectors at 650 °C; (b) $R_p$vs. ejection time (sprayed platinum nanoparticle mass) at 650 °C.

The SOFCs require that the porous electrodes have not only high charge conductivity for electrons and ions but also low resistance for gas diffusion. Due to the confined space in the electrodes, these two factors are usually competing or conflicting.[29] For example, to obtain facial gas diffusion, the larger porosity is desired for the electrodes, which can in turn reduce the effective conductivity of the electrode. Conversely, relatively smaller porosity is beneficial for improving the effective conductivity of the electrode; it will inevitably increase the resistance for gas diffusion. The ideal electrodes should have sufficient material backbone for charge transport while having enough open pores for facial gas diffusion. With relatively short spraying time of 5 seconds, the formed nanowire network can only partially cover the electrode surface (Fig. 3a). Since some of the ORR sites could not directly connect to the external circuit through the nanowire network in this case, the polarization resistance was relatively high (0.37 Ω cm^2). With the spraying time of 15 seconds, the electrode surface covered by the nanowire network was obviously increased (Fig. 3b). Accordingly the polarization resistance was reduced (0.14 Ω cm^2). Further increasing the spraying time to 20 seconds, the covered electrode surface was further improved (Fig. 3c), making the polarization resistance further decrease (0.1 Ω cm^2).With the longer spraying time of 30 seconds, the covered electrode surface with nanowire network was further improved (Fig. 3d), however, too many nanowires could block the small open pores, resulting in the increase of the gas diffusion resistance and the overall polarization resistance (0.32 Ω cm^2).

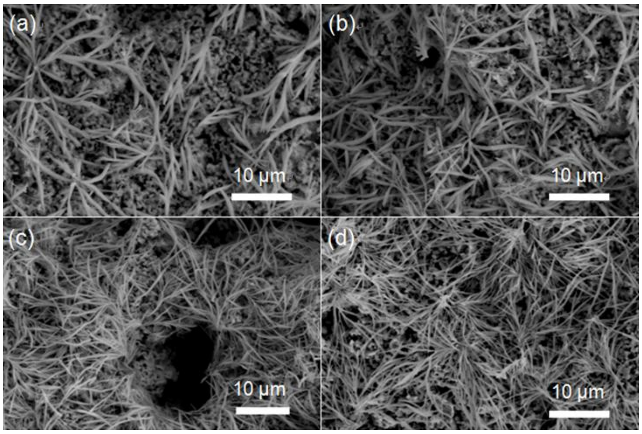

Fig. 3 The spraying time length and the resulting density distribution of platinum nanowire network on the cathode surface. (a) 5s; (b) 15s; (c) 20 s; (d) 30 s.

The electrochemical performance of the anode-supported cell NiO-SDC/SDC/PBCO was evaluated, in which the cathode current collector was fabricated by spraying the platinum nanoparticle coated carbon black ink for 20 seconds. The ambient air was used as the oxidant while the humidified H_2 (~ 3% H_2O) was supplied to the anode chamber as the fuel. As shown in Fig. 4a, the peak power density of the cell reached 1535 mW cm^{-2} at 650 °C, 1060 mW cm^{-2} at 600 °C, 601 mW cm^{-2} at 550 °C and 305 mW cm^{-2} at 500 °C, respectively. For the same cell with the conventional platinum paste current collector, the power density only reached 1114 mW cm^{-2} at 650 °C, 735 mW cm^{-2} at 600 °C and 435 mW cm^{-2} at 550 °C, respectively (Fig. 4b). This simple comparison showed that, with the nanowire network current collector, the power density of the cell was improved by 37.8% at 650 °C, 44.2% at 600 °C and 38.2 % at 550 °C respectively. The corresponding EIS of the cell with the nanowire current collector under open circuit conditions are shown in Fig. S3a†. The total polarization resistance, including both the cathode and anode polarizations, was 0.43, 0.19, 0.09 and 0.05 Ω cm^2 at 500, 550, 600 and 650 °C, respectively. For the same cell with conventional Pt paste current collector, the total polarization resistance was 0.285 Ω cm^2 at 550 °C, 0.15 Ω cm^2 at 600 °C and 0.07 Ω cm^2 at 650 °C respectively (Fig. S3b†). Since the cathode current collector is the only difference between these two cells, it is reasonable to believe that the platinum nanowire network current collector significantly reduced the cathode polarization resistance.

To demonstrate the generality and effectiveness of the nanowire network current collectors, the PBCO cathode was replaced by the widely used cathode materials of LSCF[19] and BSCF[20] respectively. As shown in Fig. 4b, with the conventional platinum paste as the cathode current collector, the power density of the anode supported cell Ni-SDC/SDC/LSCF reached 980 mW cm^{-2} at 650 °C, 624 mW cm^{-2} at 600 °C and 330 mW cm^{-2} at 550 °C respectively. With the platinum nanowire current collector, the power density reached 1292 mW cm^{-2} at 650 °C, 849 mW cm^{-2} at

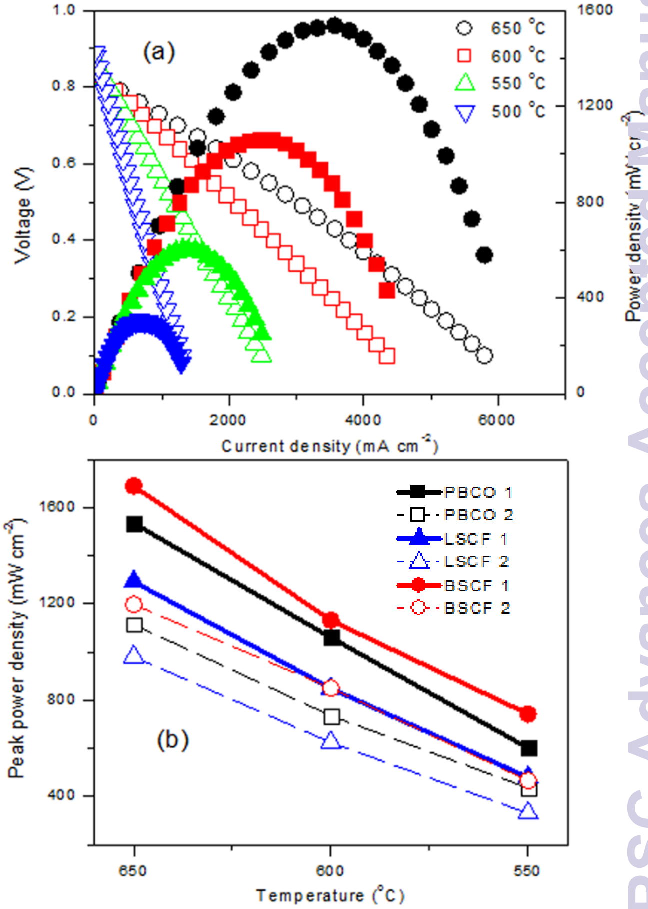

Fig. 4 (a) Performance of the anode-supported fuel cell NiO-SDC/SDC/PBCO with platinumnanowire network as the current collector; (b) The comparisons of peak power densities of anode-supported fuel cells with different cathode materials, e.g., LSCF, BSCF, PBCO, and with different current collectors: platinum nanowire network current collector (solid line), conventional Pt paste current collector (dashed line).

600 °C and 479 mW cm^{-2} at 550 °C, respectively. Accordingly the cell performance showed the improvement of 31.8% at 650 °C, 36.1% at 600 °C and 45.2% at 550 °C respectively. For the BSCF cathode, the cell Ni-SDC/SDC/BSCF also showed significant improvement of electrochemical performance. Specifically with conventional Pt paste current collector, the power density reached 1197 mW cm^{-2} at 650 °C, 850 mW cm^{-2} at 600 °C and 465 mW cm^{-2} at 550 °C, respectively. With platinum nanowire network current collector, the power density reached 1690 mW cm^{-2} at 650 °C, 1131mW cm^{-2} at 600 °C and 742 mW cm^{-2} at 550 °C respectively, an improvement of 41.2% at 650 °C, 33.1% at 600 °C and 59.6% at 550 °C, respectively.

To examine the stability of the micro-morphology of nanowire current collector and the durability of the associated cell, the long-term electrochemical test was performed for 400 hours. We considered three anode supported cells Ni-SDC/SDC/PBCO with different loadings of platinum current collectors. The loading time of platinum ink was controlled at 15 s, 20s and 25s respectively. The history of corresponding peak power density was shown in Fig. S4†. The performance degradation exhibited only 1.5%, 1.2% and 1.9% respectively. The degradation could be attributed to every single component and interface in the cell, which is beyond the scope of this paper. However, the FESEM images of the current collectors after the long term test (100 h and 400 h) did not show too much difference from those before the long term test (Fig. S5† and Fig. 1b), indicating that the platinum nanowire network current collector is feasible to improve the cell performance while achieving certain durability for intermediate temperature SOFCs.

In conclusion, a platinum nanowire network was successfully developed as an ultrathin electrochemically efficient current collector for intermediate temperature SOFCs. The unique platinum network on cathode surface can connect the ORR sites at the nano-scale to the external circuit while being able to substantially avoid blocking the open pores of the cathode. The superior electrochemical performance was exhibited, including the highly reduced electrode polarization resistance of 0.1 Ω cm^2, improved power density of 1535 mW cm^{-2} at 650 °C in hydrogen and good thermal-cycle stability. Furthermore, this novel nano-scale platinum current collector can be extensively applied to other cathode materials and cell structures while showing the capability of being scaled up for mass productions due to the easily operated spraying process.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, TGA-DSC curves, SEM comparison, impedance spectra of fuel cells, long term stability, and post-test SEM images.]. See DOI: 10.1039/b000000x/

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