Temperature-controlled growth of single-crystal Pt nanowire arrays for high performance catalyst electrodes in polymer electrolyte fuel cells

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Abstract

In the past decades, studies have been intensively conducted for the development of high performance electrocatalysts with novel nanostructures. Previous results have established that the electrocatalytic activity and durability of electrocatalysts not only depended on the ratio of surface area to volume, but also arrangements of atoms, the surface structures and their morphologies. For example, the high surface energy of extremely small nanoparticles often induces severe aggregation and Ostwald ripening, which are considered as two of the main contributors to the fast drop of power output and significant degradation of cycling life. Compared with zero-dimensional (0D) nanoparticles, one-dimensional (1D) Pt nanostructures such as nanowires, benefiting from the inherent structural characteristics like anisotropy and preferential exposure of highly active crystal facets, exhibit enhanced catalytic activity and durability [1]. For example, Lee et al. [2] synthesized single-crystal Pt nanowires (PtNWs) on Pt and W gauzes, which showed excellent catalytic activities towards oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). Liang et al. [3] prepared a free-standing Pt nanowire membrane and demonstrated that the 1D nanostructure displayed remarkably higher catalytic stability than Pt/C and Pt black.

In the synthesis of nanostructures, reaction temperature has been regarded as an important controlled factor. Controlling temperature is a good tool to tune the phase formation kinetics and the driving force for mass transfer, thus changing the morphology and property of the product. Unfortunately, up to today, most studies related to Pt nanowires only focused on a fixed temperature, because it has been usually agreed that a relative low reaction temperature is necessary to slow down the reduction rate of Pt ions, favouring the growth of {111} planes and therefore leading to the formation of single-crystal Pt nanowires. For instance, at room temperature, Sun et al. [4] synthesized single-crystal Pt nanowires on carbon black via the reduction of H_2PtCl_6 by HCOOH. At 110 °C, Xia et al. [5] grew Pt nanowires by reducing H_2PtCl_6 with ethylene glycol in the presence of polyvinyl pyrrolidone (PVP). However, in the synthesis of nanostructures, the growth temperature also plays a key role on their behavior, e.g. distribution and aggregation of nanostructures. In practical applications, the behavior of Pt nanowires is as important as the Pt nanowires themselves. For example, when Pt nanowires are used as electrocatalysts in fuel cells, they should possess an optimal distribution in the catalyst layer to achieve a low charge and mass transfer resistance, a suitable length to enable self-support, and an ultra-thin size to obtain a high electrochemical surface area. This highlights the importance of a finely tuned synthesis temperature for simultaneously controlling the behavior and structure of Pt nanowires for practical applications.

To further understand the influence mechanism of the growth temperature on the behavior and structure of Pt nanowires, in this work, we study Pt nanowire (Pt NW) growth at various temperatures at 5, 15, 25, 35, 40 and 50 ^{o}C. Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) is used as Pt precursor with formic acid as the reducing agent and a large-area 16 cm^2 carbon paper (Sigracet 35 BC GDL) as support. The as-prepared carbon paper pieces with in-situ grown Pt nanowires are directly tested as gas diffusion electrodes (GDEs) at the cathode side in H_2/air polymer electrolyte fuel cells (PEFCs). The morphology and distribution of Pt nanowires in GDEs are analyzed with a field emission scanning electron microscope (FE-SEM).

The experiment results indicate that the growth temperature plays a key role in this process. At the low temperature, the main structures obtained are huge PtNW aggregates at the corner area of the GDE piece (Fig. 1a), but very sparse at the center area (Fig. 1b), resulting in a low catalyst utilization and poor catalytic performance. An increased temperature leads to an improved distribution of Pt NWs on the support surface, e.g. at 25 ^{o}C, more Pt nanowires are grown in the center area (Fig. 1c). However, too high the reaction temperature results in the formation of nanoparticles in solution. When the temperature reaches 50 ^{o}C, it can be seen that a lot of small nanoparticles are formed and pile up on the surface (Fig. 1d). An optimal temperature is achieved at 40 ^{o}C, where uniform Pt nanowire arrays grow on the support surface, covering evenly the whole area. They have a length of 10-20 nm and a diameter

of 4 nm in average. The fuel cell testing results further confirm the best catalytic performance of the GDE grown at 40 ^{o}C (Fig. 2). A maximum power density of 0.82 W cm^{-2} was obtained at 0.6 V, higher than the state-of-the-art commercial TKK Pt/C catalyst.

Considering the power performance in practical fuel cells and the PtNW behaviour on the support surface, a possible mechanism for the influence of temperature on PtNW growth is suggested. Our improved understanding here from PtNW GDEs could provide useful reference for research on novel nanostructures in fuel cells and other catalytical applications.

References

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Figures

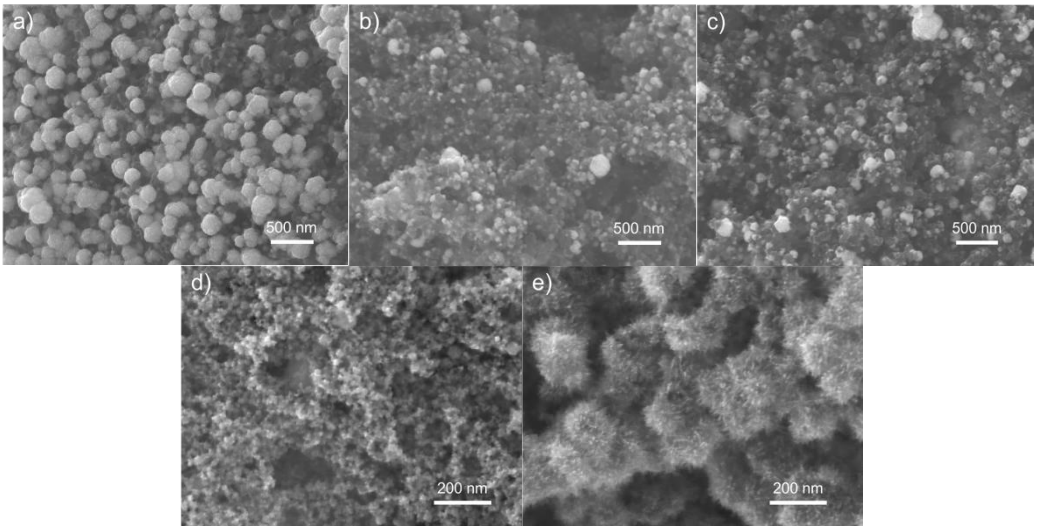

Fig. 1. SEM images of PtNW GDEs grown at (a-b) 5, (c) 25, (d) 50 and (e) 40 ^{o}C. a) shows the corner, b-e) show the center area of a 16 cm^{2} PtNW GDE.

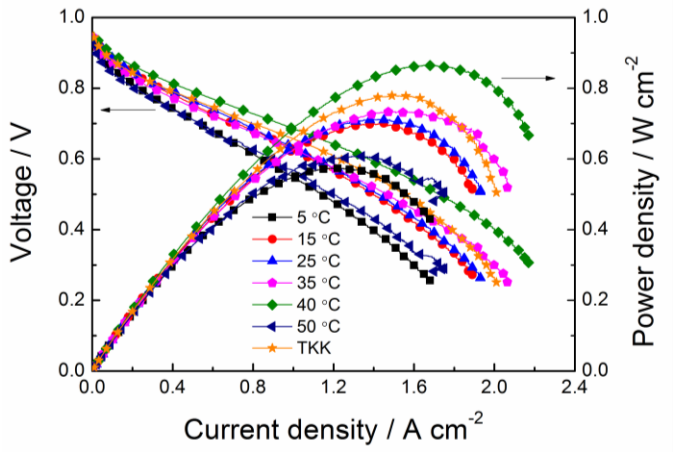

Fig. 2. Polarization and power density curves of PtNW GDEs grown at different temperatures and the one with TKK Pt/C catalyst. The polarization curves are recorded at 70 ^{o}C at a scan rate of 1 mV s^{-1}. H_2 and air gases are humidified at 75 ^{o}C with the stoichiometry of 1.3/2.4, respectively. The backpressure is 2 bars at both sides.