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Gas diffusion electrode with platinum/titanium nitride–carbon nitride nanocatalysts for the energy-saving and environment-friendly electrodeposition of manganese dioxide

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ABSTRACT

In this paper, the gas diffusion electrode with the platinum/titanium nitride-carbon nitride catalysts was used as the cathode instead of the traditional cathodes (copper and carbon) to save energy and protect the environment. X-ray diffraction, field emission scanning electronic microscopy and transmission electron microscopy were used to characterize the composition, surface structure and nanoparticle size of the platinum/titanium nitride–carbon nitride catalyst. The titanium nitride nanoparticles (20–70 nm) were embedded in the carbon nitride nanowires (30–80 nm); the platinum nanoparticles deposited on the titanium nitride–carbon exhibited good dispersion. The gas diffusion electrode with the platinum/titanium nitride-carbon nitride catalysts was also tested as a cathode in the electrodeposition of the manganese dioxide at 100 A m^{-2} in an electrolyte of 120 g dm^{-3} manganese sulfate +30 g dm^{-3} sulfuric acid at 80 °C. The results demonstrated that electrolysis was performed at 0.7 V, which decreased energy consumption by more than 60% compared with the traditional cathodes (copper and carbon). The durability of the gas diffusion electrode with the platinum/titanium nitride-carbon nitride catalysts (1500 h) is 3.3 times as long as that of gas diffusion electrode with carbon-supported platinum catalysts. After evaluation, the gas diffusion electrode with the platinum/titanium nitride–carbon nitride catalysts shows great potential for the energy-saving and the environment-friendly electrodeposition of manganese dioxide. The platinum/titanium nitride-carbon nitride catalyst may be promising candidate for fuel cells in the future because of its high activity and durability.

1. Introduction

The electrolytic manganese dioxide (EMD) has been widely used as an active electrochemical electrode material, with major applications in Li^- batteries (Dose and Donne, 2013), alkaline batteries (Biswal et al., 2016), and supercapacitors (Prasad and Miura, 2004), because of its high discharge rates and long storage life (Maphanga et al., 2009). EMD is used as green energy storage material with an annual output value of 465,900 metric tons worldwide; China alone contributes ~64.02% (Biswal et al., 2015a). China has the largest EMD industry in the world but it is a classic high-energy-consuming and air-polluting industry.

The energy consumption of the electrodeposition of MnO_2 in China is ~495,126,839 kWh (Tang et al., 2014). Coal plays a bigger role than oil in China (Alwi et al., 2014); thus the electrodeposition of MnO_2 will consume ~157,450 t coal per year in China (Yuan et al., 2016). The by-product of EMD is hydrogen gas, which produces considerable quantities of acidic fog into the air. The acidic mist threatens health, and pollutes the environment. The electrodeposition of MnO_2 consumes nine times more energy than steel production (Guo and Fu, 2010). Consequently, the unsolved problems associated with high energy consumption and environmental pollution hinder the widespread application of MnO_2. To tackle these problems, some new technologies have been proposed to reduce the energy consumption of MnO_2. Recent work by Biswal et al. (Biswal et al., 2015b) provides a novel method for electrodeposition of MnO_2, with stainless steel as the cathode and the addition of unique non-ionic surfactant (Pluronic F127) and activated carbon in solution. Their method can decrease energy consumption from 1.696 kWh/kg to 1.501 kWh/kg and save energy by

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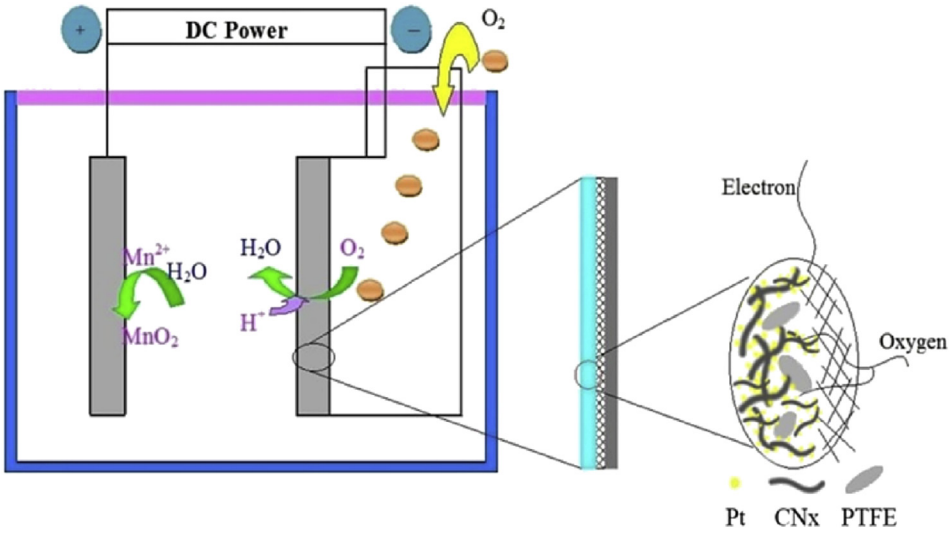

Fig. 1. The schematic diagrams of the Pt/TiN–CN_X GDE electrolysis.

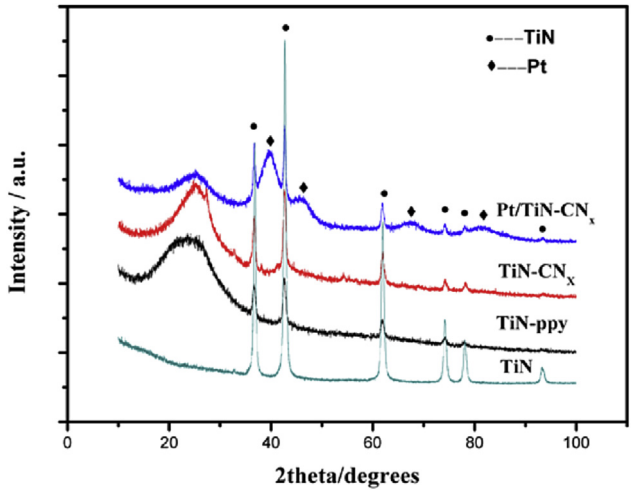

Fig. 2. XRD patterns of Pt/TiN-CN_X, TiN-CNx, TiN-PPy and TiN.

11.5%.

In our previous work, a Pt/C gas diffusion electrode (GDE) was used as the cathode instead of traditional cathodes in the electrodeposition of MnO_2. In theory, when the Pt/C GDE is applied, the oxygen reduction reaction (ORR) replaces the hydrogen evolution reaction, as shown in Equations (1)–(3) (Tang et al., 2015)

$$\text{Anode: } Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \; E^0 = 1.23 \text{ V vs.} \quad (1)$$

$$\text{Traditional cathode: } 2H^+ + 2e^- \rightarrow H_2 \; E^0 = 0 \text{ V vs. SHE} \quad (2)$$

$$\text{GDE as cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \; E^0 = 1.229 \text{ V vs. SHE} \quad (3)$$

The electric energy savings with the Pt/C GDE during the electrodeposition of MnO_2 is theoretically 99%. However, the electric energy decreases from 1.1872 kWh/kg to 0.45 kWh/kg at 100 A m^{-2}. Thus, the Pt/C GDE can save electric energy by ~62% (Tang et al., 2014). Because the ORR at the Pt/C GDE can mainly proceed via the $4e^-$ reduction of oxygen to water (Tang et al., 2015). However, the durability of the Pt/C GDE for the energy-saving and environment-friendly electrodeposition of MnO_2 should be improved.

GDE is mainly used in fuel cells (Hezarjaribi et al., 2014) or in the presence of alkaline and neutral solutions such as chlor–alkali electrolysis (Ichinose et al., 2004), the electrolysis of potassium iodine (Tang et al., 2012), and the electrolysis of sodium carbonate (Tang et al., 2013) to save energy and protect the environment. To our knowledge, the durability of the GDEs has been studied in chlor-alkali electrolysis but not in the electrolysis of potassium iodine or the sodium carbonate. In chlor–alkali electrolysis, Pt/C GDE can be used for 300 days (Furuya and Aikawa, 2000). However, the durability of Pt based GDE in acidic medium and fuel cell is much lower, compared with chlor–alkali electrolysis. For fuel cells to be commercially viable, several technical barriers need to be overcome. The durability of GDE is a key issue. Some efforts have been made to study the failure mechanism of the Pt-based GDE in fuel cells. Galbiati et al. (Galbiati et al., 2013) synthesized a Pt alloy catalyst that could be used in phosphoric acid-doped polymer fuel cells for 70 h, but the voltage was reduced by Pt dissolution and carbon corrosion. According to Park et al. (Park et al., 2016), the durability of Pt/CB for proton exchange membrane fuel cell was 100 h because of agglomeration of the Pt nanoparticles. These studies have improved our understanding of the importance a catalyst in the GDE. Therefore, the low stability of the Pt-based catalyst is one of the major challenges that hinder the large-scale implementation of these fuel cells (Zeng et al., 2014).

In our work, the platinum/titanium nitride–carbon nitride (Pt/TiN–CN_X) catalyst was first synthesized by a chemical method and used to prepare the GDE. The Pt/TiN–CN_X GDE was successfully used in acidic medium for the energy-saving and environment-friendly electrodeposition of MnO_2. The Pt/TiN–CNx GDE exhibited high activity (~0 V vs. Hg/$HgSO_4$) and durability.

2. Experimental

The morphologies of the catalysts were measured by field emission scanning electron microscopy (FESEM; SUPRA55) and high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F30). X–ray diffraction (XRD) was conducted with the Ultima VI with Cu Kα radiation at 40 kV and 40 mA to determine the chemical composition and structure of the catalysts. X-ray photoelectron spectroscopy (XPS) using AXIS U1tra with a monochromatic Mg Kα radiation was used to determine the elemental concentration of the