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RESEARCH PAPER

Oxidation of formic acid over palladium catalyst supported on activated carbon derived from polyaniline and modified lignosulfonate composite

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Abstract: Activated carbons (AC) were obtained through carbonization of polyaniline and modified lignosulfonate composite (PAn-MLS) under different temperatures; they are characterized by Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, nitrogen sorption and scanning electron microscope (SEM). With these carbon materials as the support, a series of Pd-AC catalysts for the oxidation of formic acid were prepared by liquid phase reduction and characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and electrochemical analysis. The results show that with the activated carbon prepared at 800°C (AC800) as the support, the Pd-AC800 catalyst obtained performs best in the oxidation of formic acid; the palladium particles have an average size of 5.4 nm and the electro-active surface area reaches 53.78 m^2/g. As the oxidation of formic acid over Pd-AC800 is realized through direct pathway rather than CO pathway, Pd-AC800 may be considered as a potential electrode material in direct formic acid fuel cells (DFAFC).

Key words: polyaniline; modified lignosulfonate; activated carbon, Pd-AC; formic acid; oxidation; direct formic acid fuel cells

Nowadays, the excessive consumption of fossil fuel has brought great concerns on the ecological environment. Petroleum, coal and natural gas resources have been exhausted increasingly and it is urgent to adjust current energy structure[1]. Clean energy, which is environment-friendly and recyclable, has accounted for a higher and higher proportion in the future energy frame[2]. Direct Formic Acid Fuel Cell (DFAFC) is a promising application among alternative clean energies, owing to the excellent electrochemical oxidation performance of formic acid[3].

Palladium as a noble metal catalyst component has been widely used in petrochemical industry[4], environmental protection, organic synthesis and pharmaceutical industry[5]; it is also regarded as the most suitable catalyst for the oxidation of formic acid in DFAFC[6]. Activated carbons are the most conventional support as electrode material[7]. The performance of activated carbon supported Pd catalyst is largely related to the properties of the support[8,9]; activated carbon with proper structure can reduce the metal loading and prevent the aggregation of Pd. As a result, various activated carbon materials have been proposed as the support for Pd catalyst. Wang et al[10] have modified the activated carbon support for Pd catalyst in CO oxidation by using different pretreatment methods. In Chen et al's[11] research, activated carbon functionalized with diaminocyclohexane groups has been used for the preparation of the supported Pd alloy.

Polyaniline (PAn) can be used as a precursor to prepare activated carbons, which can retain the molecular bones and provide abundant nitrogen elements. As a particular aromatic compound, PAn possesses 79% carbon and 15% nitrogen and has aroused much attention because of its low cost, easy synthesis, high conductivity and corrosion resistance[12,13]. It has been reported that the nitrogen-containing functional groups play a significant role in improving wettability of nanomaterials and dispersion of adsorbates[14]. More and more polyaniline composites, with special structures and abundant functional groups, have been used to prepare activated carbons. For instance, polyaniline-poly (styrenesulfonate) hydrogels were pyrolyzed to obtain activated carbons for the adsorption of vitamin B12 by Jia et al[15].

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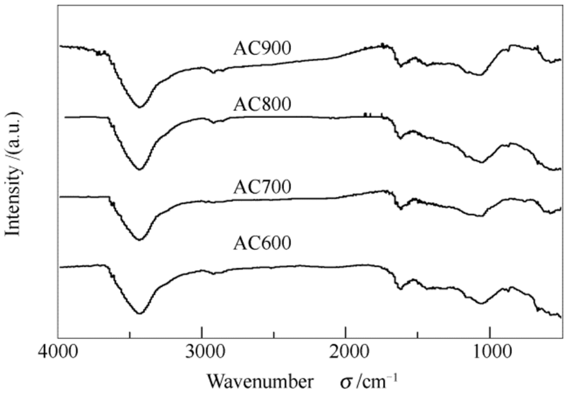

Fig. 1 FT-IR spectra of AC600, AC700, AC800 and AC900

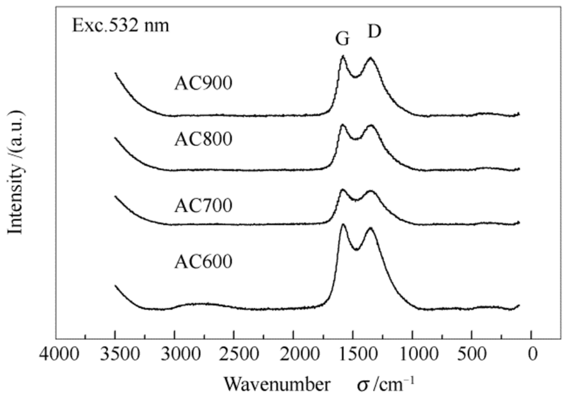

Fig. 2 Raman spectra of AC600, AC700, AC800 and AC900

Lv et al[16] have prepared the novel nitrogen-containing hollow carbon nanospheres by direct pyrolysis of the polyaniline-lignosulfonate composite spheres to adsorb papain.

In this work, polyaniline-modified lignosulfonate composite (PAn-MLS) has been prepared by in-situ polymerization; the composite was then calcined under inert atmosphere to get activated carbons (AC). With the activated carbon as support, Pd-AC catalysts were prepared and used in the oxidation of formic acid.

1 Experimental

1.1 Reagents and chemicals

Aniline monomer (An, Beijing Chem. Co., China) was distilled under reduced pressure before use. Sodium lignosulfonate and $PdCl_2$ were of analytical grade and used without further purification. All the solutions were prepared with distilled water.

1.2 Preparation method polyaniline-modified lignosulfonate (PAn-MLS) based activated carbon

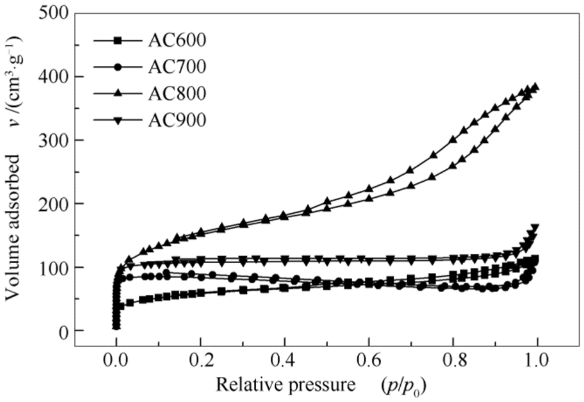

Fig. 3 N_2 adsorption-desorption isotherms of AC600, AC700, AC800 and AC900

Lignosulfonate was first oxidized by H_2O_2 and then reacted with formaldehyde and sodium sulfite to get modified lignosulfonate (MLS). The PAn-MLS composite was then synthesized by in situ polymerization. After that, PAn-MLS powders were heated in nitrogen to a certain carbonization temperature (600, 700, 800 and 900°C) at a heating rate of 5°C/min and maintained at this temperature for 2 h. After cooling down to the room temperature, the PAn-MLS based activated carbons obtained were washed by distilled water and dried; depending on the carbonization temperature, they are marked as AC600, AC700, AC800 and AC900 in this work.

Pd catalyst. At room temperature, 80 mg AC600 was mixed with 8.33 mL 0.02256 mol/L $PdCl_2$ solution and 10 mL H_2O. After 1 h ultrasonic treatment, the mixture was stirred for 4 h. Na_2CO_3 solution was used to adjust the pH value of the mixture to 8.0–9.0. After that, excessive $NaBH_4$ solution was added by drops to reduce the Pd ions and another 2 h continuous stirring was used to ensure a complete reaction. The resultant Pd catalyst was filtered and washed and finally dried in a vacuum oven at 60°C; they are marked as Pd-AC600, Pd-AC700, Pd-AC800 and Pd-AC900, depending on the carbonization temperature to get the AC support. As a comparison, Pd supported on the coconut shell activated carbons carbonized at 800°C (Pd-CAC800) was also prepared, with the same process and Pd loading as those for Pd-AC.

1.3 Characterization

Fourier-transform infrared spectra (FT-IR) of the samples were obtained on an IS100 spectrometer (Nicolet, USA). The morphology of samples was determined by transmission electron microscope (TEM) on and scanning electron microscope (SEM) on JEM-2100 (JEOL Ltd., Japan). Scanning electron microscopy spectrum was obtained by 3400-I (Hitachi, Japan). Raman spectra were recorded on a Thermo Scientific DXR (USA). X-ray diffraction (XRD) was taken with a Bruker D8FOCUS diffractometer (Germany).