Synthetic Metals 160 (2010) 2191–2196

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Pure carbon microwave absorbers from anion-exchange resin pyrolysis

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ARTICLE INFO

Article history:
Received 13 July 2010
Received in revised form 8 August 2010
Accepted 10 August 2010
Available online 15 September 2010

Keywords:
Pure carbon materials
Microwave absorber
Anion-exchange resin
Reflection loss
Nanocrystalline graphite

ABSTRACT

A series of carbon materials [C_F-*x* (where *x* denotes carbonization temperature)] have been prepared by pyrolysis of an anion-exchange resin at different temperatures (500–700 °C). X-ray diffraction and Raman spectroscopy suggest the presence of tiny crystalline domains in these materials, whose content is strongly determined by carbonization temperature. The microwave absorption of these materials is examined in the frequency range of 2–18 GHz, and it is found that the reflection loss characteristics are highly sensitive to the carbonization temperature. At a thickness of 2 mm, C_F-600 exhibits the best microwave absorbing ability with a maximum reflection loss of −20.6 dB at 16 GHz, and a bandwidth exceeding −10 dB in the range 13.5–18 GHz. It is concluded that dielectric loss in cooperation with better matched characteristic impedance results in the excellent microwave absorption of C_F-600. Furthermore, a reflection loss exceeding −10 dB can be obtained in the range of 7–18 GHz by manipulating the thickness from 2 to 3.5 mm, and the maximum can reach −37.0 dB at 10.8 GHz with a thickness of 2.8 mm. These materials may be used as light-weight and highly effective microwave absorbers over a wide frequency range.

1. Introduction

Rapidly expanded applications of electromagnetic waves in civil and military fields have caused a series of problems in electromagnetic interference, human health, environmental pollution, etc. To solve, or at least decrease the above problems, numerous efforts have been devoted to the investigation of efficient and pertinent microwave absorbers. Previously, magnetic materials (metals, alloys and ferrite species) and some ternary oxides ($BaTiO_3$) were used as major microwave absorbers [1–4], and showed well properties in microwave absorption. However, high specific gravity and difficult formulation have limited their practical applications [5]. Therefore, although lots of efforts have been made in this field, it is still desirable to explore novel microwave absorbers that have light weight with effective absorption over a wide frequency range.

In recent years, carbon-based microwave absorbers have attracted more and more interest due to their tunable properties, relative low density, abundant resource, easy preparation, and low cost. And couples of reports have pointed out that carbon-based materials could be good candidates for novel microwave absorbers [6–25]. For example, carbon nanotubes, graphite, graphite oxide and carbon fibers are commonly used as carbon-based microwave absorbers [6–19]. Unfortunately, these pure graphitic carbon materials have too much high surface resistance to transmit the microwave into the materials, arising from the large difference between complex permittivity and complex permeability, which is far away from the zero-reflection condition at the surface of the materials and always results in poor absorption [13]. To solve this problem, many scientists had to combine these carbon materials with various magnetic particles, which can reduce the complex permittivity and enhance the complex permeability, to produce well microwave absorbing abilities in certain frequency range [6–19], but this process will drastically increase the density of carbon materials. As another allotrope of carbon, amorphous carbon materials exhibit versatile properties in many fields, however, which are seldom applied as microwave absorbers due to too low complex permittivity to consume the energy of microwave. Although microwave absorption of composites of magnetic particles and amorphous carbon are reported [20–22], amorphous carbon only appears as the support to disperse magnetic particles and reduce the eddy current loss, that is, most contribution of microwave absorption actually comes from the magnetic particles rather than amorphous carbon [20–22]. Obviously, a pure carbon microwave absorber should be sought from the transition state between graphitic carbon and amorphous carbon, which can be greatly helpful for the development of light-weight microwave absorbers. For example, carbon microcoils and nanocoils prepared by high temperature catalytic decomposition organic vapors (acetylene, benzene or methane) have been reported as good microwave

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doi:10.1016/j.synthmet.2010.08.008

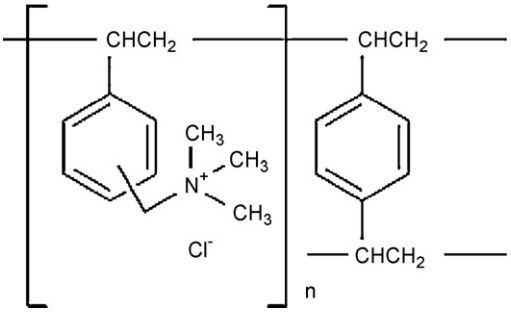

Fig. 1. The basic structure of a polystyrene strong-base anion-exchange resin (PSAR).

absorbers even in the absence of magnetic particles [23–28], whose unique physical properties and low graphitic degree were considered to be responsible for their excellent microwave absorption. Nevertheless, relatively rigorous conditions and manipulation may restrict their further applications.

Recently, various ion-exchange resins were widely utilized as carbon source to produce good absorbents, catalysts and catalyst supports because of their low costs and feasibility for large-scale manufacturing [29–32]. To our knowledge, there is still no report on the microwave absorbing properties of carbon materials from resin pyrolysis. In this article, we synthesized a series of carbon materials [C_F-*x* (where *x* is the carbonization temperature)] by pyrolysis of an anion-exchange resin at different temperatures (500–700 °C), and the microwave absorbing properties of obtained products were examined in detail. Very interestingly, the optimum sample (C_F-600) produces fairly good microwave absorption in the absence of any magnetic particles, whose reflection loss exceeding −10 dB can be obtained in the range of 7–18 GHz by manipulating the thickness from 2 to 3.5 mm, and the maximum reflection loss can reach −37.0 dB at 10.8 GHz with a thickness of 2.8 mm.

2. Experimental

2.1. Sample preparation

Commercial polystyrene strong-base anion-exchange resin (PSAR) was chosen as the carbon source, and the basic structure is shown in Fig. 1. In a typical synthesis, 15 g of PSAR was mixed with 100 ml of 0.15 M $K_3[Fe(CN)_6]$ aqueous solution to obtain the corresponding resin derivatives. After 1 h, the resin derivatives were collected by filtering, washing with distilled water, and drying at 60 °C. The dried resin derivatives were carbonized in a horizontally tubular furnace under N_2 atmosphere at different temperatures for 4 h with a heating rate of 2 °C/min. Then, the obtained products were refluxed in hot HCl solution to remove the residual Fe species. Final products were denoted as C_F-*x*, where *x* refers to the carbonized temperature.

2.2. Characteriztion

Powder X-ray diffraction (XRD) data were recorded on an XRD-6000 X-ray diffractometer (Shimadzu) with a Cu Kα radiation source (40.0 kV, 30.0 mA). X-ray photoelectron spectroscopy (XPS) was recorded at room temperature in a PHI 5700 ESCA system. Scanning electron microscope (SEM) images were obtained on the S-4800 (Hitachi) scanning microscope, and the samples were mounted on aluminum studs using adhesive graphite tape and sputtered coating with gold before analysis. Raman spectra were performed on a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. A HP-5783E vector network analyzer was applied to determine the complex permeability and permittivity in the frequency range of 2–18 GHz for the calculation of reflection loss. A sample containing 60 wt.% amorphous carbon powders was pressed into a ring with an outer diameter of 7 mm, an inner diameter of 3 mm, and a thickness of 2 mm for microwave measurement in which paraffin wax was used as the binder.

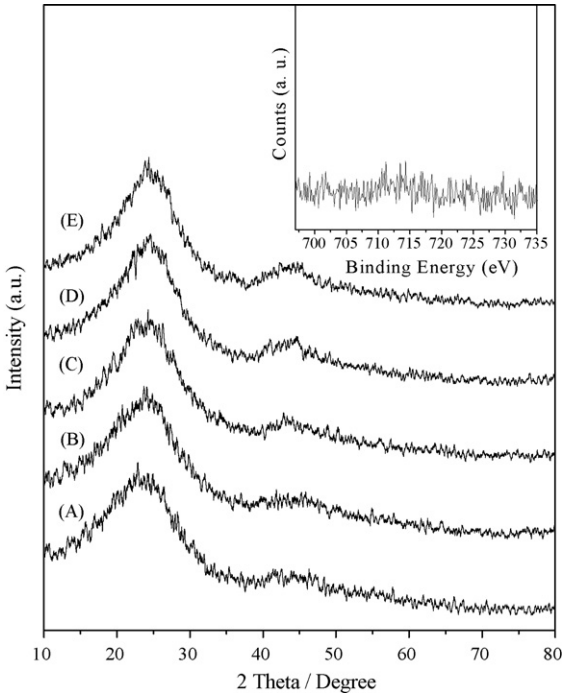

Fig. 2. The XRD patterns of C_F-500 (A), C_F-550 (B), C_F-600 (C), C_F-650 (D) and C_F-700 (E). Inset is the XPS spectroscopy of C_F-600.

3. Results and discussion

Fig. 2 shows the XRD patterns of C_F-*x* (*x* = 500–700) from different carbonization temperatures. Notably, all samples exhibit a very broad diffraction peak centered at 24.2°, indicating the amorphous nature of these carbon materials [33]. With increasing the carbonization temperature, especially for C_F-600, C_F-650, C_F-700, there is a slight increase in the intensity of the peak at 44.2°, which can be attributed to the formation of tiny crystalline domains at the surface of the materials [34]. However, these tiny crystals are very difficult to detect, even undetectable by high-resolution transmission electron microscopy (HR-TEM) [34]. Additionally, no peaks indexed to Fe species can be observed, suggesting that most of Fe species have been removed. This conclusion can be further supported by the XPS spectroscopy, although this technique is quite sensitive to trace elements, there are still no obvious peaks that can be assigned to Fe species (Fig. 1, inset).

As a typical sample, Fig. 3 shows the SEM images of C_F-600. Obviously, the sample is composed of irregular bulky particles (Fig. 3A), and there are some random crackles on the surface of these particles (Fig. 3B), which may be produced by the shrinkage of carbon species during the carbonization process.

Raman spectroscopy is widely used for characterizing the structure of carbonaceous materials by examining the bonding state of carbon atoms in the given materials. As shown in Fig. 4, all samples display two distinguishable peaks in the range of 1000–2000 cm^{-1}, one is a broad peak centered at about 1350 cm^{-1} (*D* band), the other is a relatively sharp peak at about 1590 cm^{-1} (*G* band). Also, it has been found that the value of the intensity ratio of these two bands, I_D/I_G, monotonously increases from 0.65 to 0.80 with the increase of carbonization temperature. The *D* band and *G* band were once