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Solid waste for energy storage material as electrode of supercapacitors

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ABSTRACT

We propose a novel idea to utilize environment pollutant cigarette ash for energy storage material as electrode of supercapacitors as supercapacitors can deliver high power and reasonable energy densities as compared to batteries which deliver energy as a result of chemical reactions and suffer with low power densities. Keeping in view this advantage and research focus in this field, supercapacitors of cigarette ash were fabricated as energy storage devices. The electrode composed of ash shows specific capacitance of 183.33 F/g at current density of 1 A/g for 1st cycle and 165 F/g for 2000th cycle which indicate its remarkable long-term cyclic stability in Na_2SO_4 electrolyte.

1. Introduction

Global warming is ever increasing at an alarming rate with increasing fossil fuel based power consumption. The residues or by-products of these fuels have been a constant threat to ecological system. It is important to develop environment friendly energy production methods with minimal by-products and 100% conversion efficiency. Several facile methods have been proposed to address the issue of ever increasing pollution including energy production from rice husk, dead leaves and other waste derived materials [1–10]. One of the major contributors in pollution is smoking ash which can be successfully used to store and produce large amount of energy in supercapacitors.

Supercapacitors are an excellent alternative to traditional methods of energy storage like batteries and dielectric capacitors. On contrary to traditional double layer capacitors, pseudo-capacitors can achieve high levels of energy storage. Recent reports have established that 'the redox reaction' in metal oxides can be successfully used for this type of storage phenomenon [5–10]. Although these metal oxides have shown higher performances but their application is limited due to their instability and small scale production. The stability and large scale production of these oxides with tuned structures is rarely demonstrated [11–28]. Different combinations of metals can be used to achieve tunability in stoichiometric/non-stoichiometric compositions like Ni-Co based $NiCo_2O_4$ which has provided efficient electrochemical performance and extraordinary stability.

Smoking ash inherently consists of a mixture of calcium, potassium and magnesium carbonates. These carbonates can be applied for energy storage applications. Here, we demonstrate supercapacitors based on smoking ash which shows excellent energy storage capacity (183.5 F/g@1 A/g) through pseudocapacitance and high cyclic efficiency (2000 cycles with over 90% capacity retention).

2. Experimental section

In order to collect cigarette ash, the cigarettes were lit and fixed at one end of a plastic pipe and the other end was connected to a mechanical rotary pump in open environment; air was sucked

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through the cigarette with the mechanical rotary pump. Ash was collected in a beaker as the cigarettes were smoked.

The structure and the phase of the cigarette ash was determined by X-ray powder diffraction (XRD, Philips X'Pert Pro MPD) with Cu Kα radiation whereas the morphologies of the products were examined by scanning electron microscopy (SEM, Hitachi S-3500). The chemical composition and energy states were determined by energy dispersive spectroscopy (EDS) and XPS (X-ray Photoelectron Microscopy) analysis respectively.

(Preparation of electrodes is presented in Supporting information).

3. Results and discussion

3.1. Structure and composition of cigarette ash

XRD analysis is presented in Fig. 1(a) which confirms the existence of metallic components. It can be depicted that the cigarette ash is mainly composed of $CaCO_3$ (calcite) with traces of its mixed carbonate with potassium named as potassium calcium carbonate. A small amount of the magnesium silicate was also detected from XRD results. It is obvious from XRD spectra that cigarette ash is composed of various species. The main peak with highest intensity located at $2\theta=29.396°$ and many other calcite peaks suggest that the main component is calcium carbonate. All the peaks of calcium carbonate correspond to JCPDS card no. 01-072-1937 and suggest the rhombohedral crystal structure of calcite with lattice parameters a=4.9870 nm and c=17.08 nm. Hexagonal potassium calcium carbonate with lattice parameters a=5.2940 nm and c=13.3550 nm correspond to JCPDS card No. 00-021-1287. Orthorhombic magnesium silicate with lattice parameters a=18.2110, b=8.8100 and c=5.2030 correspond to JCPDS card no. 01-073-1937.

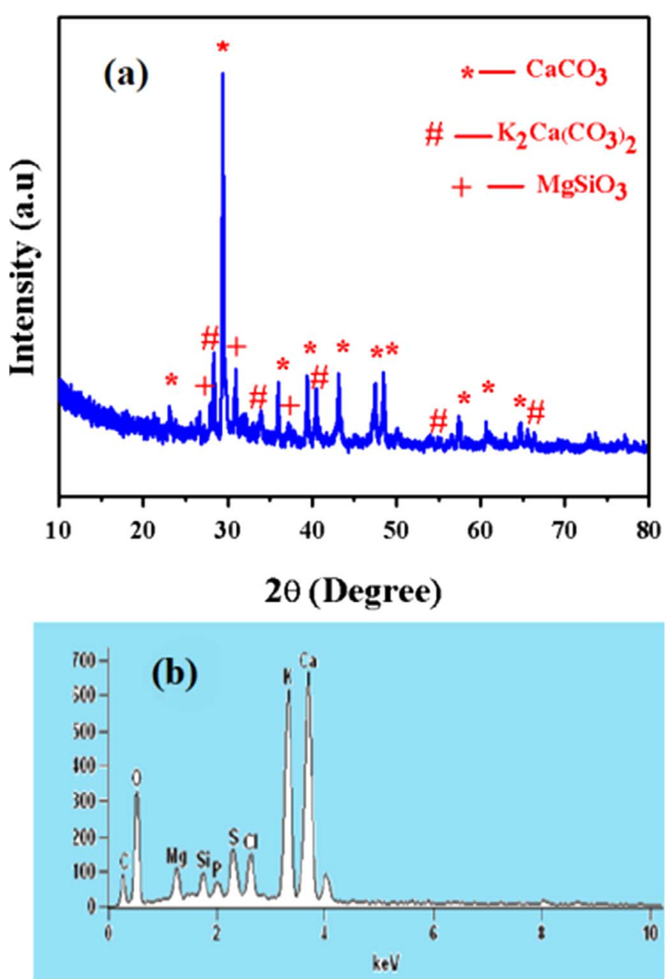

Fig. 1. (a) XRD spectrum (b) EDS profile of cigarette ash.

In order to confirm the XRD investigations and to determine the chemical composition, EDS analysis was performed as shown in Fig. 1(b). EDS results reveal that calcium is present up to 10% in the ash. Potassium has more than 7% elemental ratio and carbon is 30% in the composition. However, oxygen exists as the major constituent up to 45% because it is the basic element of carbonates and silicates present in the ash.

Thermal gravimetric analysis (TGA) was performed to determine its stability and composition. There are several decomposition phases for smoking ash as shown in Fig. 2 including a couple of small weight losses followed by major degradation around 620 °C. The first decomposition appears around 150 °C which can be attributed to loss of trapped water molecules. Next small decomposition is due to removal of residual carbon present in ash through the oxidation process as TGA studies were carried out in ambient air. Since major content of ash consist of metal carbonates like calcium carbonate (decomposition temperature >800 °C), calcium potassium carbonate and silicates (Magnesium silicate (decomposition temperature >800 °C) suggested by Martin et al. which are very difficult to decompose at lower temperatures [21]. So, the weight loss at 620 °C is due to decomposition of binary metallic carbonate resulting in formation of potassium and calcium carbonates respectively.

To explore the chemical states of elements and composition of cigarette ash, XPS was performed and results are presented in Fig. 3. The existence of the core levels of carbon, oxygen, calcium and potassium is confirmed and shown in Fig. 3(a). Fig. 3(b) shows high resolution spectra of C 1s with three main peaks at different binding energies suggesting that carbon is present in different chemical states in ash. The first peak present at 283.5 eV corresponds to elemental carbon because of burned cigarette paper and peak present at 291.4 eV corresponds to its compound form as calcium carbonate while at 293.9 eV is related to potassium calcium carbonate. The peak of small intensity present at 287.84 eV corresponds to SiC.

Calcium doublets of Ca 2p are well resolved in XPS analysis presented in Fig. 3(c). The peaks positions at 345.39 and 348.9 eV suggest that calcium is present in the form of calcium carbonate.

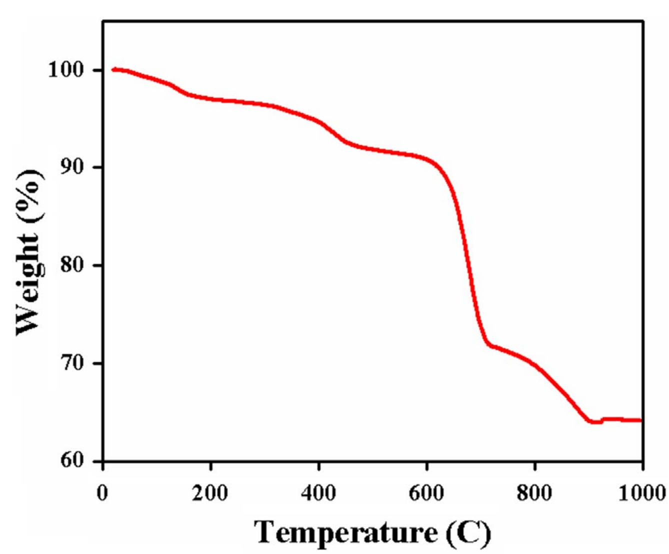

Fig. 2. Thermal Gravimetric Analysis (TGA) of smoking ash.