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Corrosion and thermal stability of multi-walled carbon nanotube–graphite–acrylonitrile–butadiene–styrene composite bipolar plates for polymer electrolyte membrane fuel cells

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HIGHLIGHTS

- ► Development of ABS–graphite–MWNT composite bipolar plates.
- ► EIS successfully applies for understanding the corrosion mechanism of the composites.
- ► MWNT concentration strongly affects the corrosion behavior of the ABS–graphite composites.
- ► The best balance of properties was for the ABS-graphite composite with addition of 2 wt.% MWNT.

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ABSTRACT

Composite bipolar plates based on the proper mixing of multi-walled carbon nanotubes (MWNTs), synthetic graphite particles and acrylonitrile–butadiene–styrene (ABS) powder have been produced by hot compression molding. The corrosion properties of the molded plates were assessed through electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves. Through-plane and in-plane electrical conductivities were determined. The relevance of electrochemical oxidation to the electrical conductivity of the composites was assessed by cyclic voltammetry. Thermal stability of the composites was examined by thermogravimetric analysis (TGA). The morphology of fractured surfaces of the plates was observed by scanning electron microscopy. The incorporation of MWNTs increased the in-plane and through-plane electrical conductivity of the ABS–graphite composites. There was, though, a corresponding reduction of the corrosion resistance. The thermal behavior was little affected by the addition of MWNTs.

1. Introduction

The development of composite bipolar plates for PEM fuel cells is a fertile research area for materials scientists [1]. In spite of the expressive accumulation of knowledge on the complex structure–property relationship of these components, several aspects are yet unexplored [2]. Corrosion resistance is an example. While metallic materials concentrate most part of the scientific investigations concerning the corrosion behavior of bipolar plates [3–6], this aspect is often disregarded for polymer–graphite composites. Such incipient research activity emerges because of the notorious chemical stability of carbon-based materials in the typical acid and humid environment of PEM fuel cells when compared to metallic alloys [7,8]. Nevertheless, it has been shown that composite bipolar plates do interact with the PEM fuel cell environment and are not immune to chemical degradation during operation. Kakati et al. [9] investigated the corrosion resistance of a composite bipolar plate prepared from a mixture of phenolic resin, graphite, carbon black and carbon fibers. They reported that the corrosion current density increased with the addition of the conductive carbon black and carbon fiber fillers. Carbon black is susceptible to electrochemical oxidation in the PEM fuel cell environment [10–12]. This chemical instability arises from the presence of numerous dangling bonds and defects in carbon blacks which are easily oxidized, leading to a high corrosion rate [13,14]. Recently, Antunes et al. [15] evidenced the deleterious effect that the incorporation of carbon black has on the corrosion stability of poly(vinylidene fluoride)–graphite composite

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in a typical PEM fuel cell environment. The growing quest for increasing electrical conductivity of polymer–graphite composites by incorporating minor carbon-based conductive fillers such as carbon black, carbon nanotubes and carbon fibers adds new issues to this scenario. As the electrical conductivity increases the corrosion resistance is expected to lessen. The correct balance between these two properties is a central point to guarantee the long-term stability of the composite bipolar plate. In this regard, the composite formulation must be carefully designed to give the best compromise between electrical conductivity and chemical stability.

Carbon nanotubes have been successfully incorporated as minor conductive fillers into polymer–graphite composites in order to enhance their electrical response for bipolar plate purposes [16–18]. Unlike carbon blacks, carbon nanotubes are resistant to electrochemical oxidation in H_2SO_4 solutions [19]. This result was perceived by several authors either at room temperature or at typical PEM fuel cell operating temperatures [20,21]. Shao et al. [22] explained this behavior by the difficult access of oxygen atoms to the closed rolled up coaxial graphene sheets of carbon nanotubes. Hung et al. [23] used electrochemical quartz crystal microbalance to assess the mass change induced by corrosion of carbon blacks and MWNTs in deaerated H_2SO_4 solution at room temperature. They showed that the highly ordered graphitic structure of MWNTs provided better corrosion resistance than the more amorphous conventional carbon black particles. It is worth mentioning that the vast majority of the studies regarding the electrochemical response of carbon nanotubes in PEM fuel cells simulating environments are based on its application as carbon catalyst supports [24,25]. However, if one thinks of the effect that these materials would have on the corrosion properties of composite bipolar plates, little knowledge is available. Moreover, it is well-established that metallic bipolar plates submitted to electrochemical polarization present a reduction of electrical conductivity [26,27]. Nevertheless, this effect has not been investigated for polymer–graphite composite bipolar plates either with CNT addition or not. Fukutsuka et al. [28] gave an interesting contribution on this subject. They determined the interfacial contact resistance of a carbon-coated austenitic stainless steel bipolar plate before and after polarization measurements. The results showed that the interfacial contact resistance of the carbon-coated bipolar plate was little affected by the polarization test whereas the bare substrate presented a significant loss of conductivity after polarization. Thus, the conductivity of the carbon surface was not impaired by the potentiodynamic polarization test.

Thermal stability is of prime interest for polymer–graphite composite bipolar plates. Polymeric matrices should withstand long-term operating conditions at temperatures typically ranging from 60 °C to 80 °C [29]. The development of high temperature PEM fuel cells may even increase the optimal service temperature of these devices, demanding further enhancements for the thermal performance of the polymers employed in the manufacturing of composite bipolar plates [30]. Both thermoplastic [31] and thermosetting resins [32] have been considered for the manufacturing of these devices. When a thermoplastic polymer is used, the composite must be cooled before being removed from the mold. Alternatively, when a thermosetting binder is used, the cooling step is not necessary and shorter processing times can be achieved [33]. This gives an irrefutable advantage of thermosetting resins toward the cost target of the Department of Energy of the US (DOE) [34]. However, recent developments have been conducted on manufacturing methods, yielding the production of high performance thermoplastic-based plates at short processing times [35]. Recyclability is considered an advantage of thermoplastics over thermosets [36].

Acrylonitrile–butadiene–styrene (ABS) copolymer provide high thermal stability with good mechanical properties, chemical resistance and processability at a relatively low cost if compared with other commercially available high performance thermoplastic resins such as polyphenylene sulfide (PPS) or polyvinylidene fluoride (PVDF) [37,38]. Notwithstanding, ABS-based composite bipolar plates have been hardly considered for this application [39]. This work gives an unprecedented contribution on the evaluation of this material for bipolar plate purposes, regarding specially its corrosion stability and thermal degradation resistance.

In this work we prepared MWNT–ABS–graphite composites using compression molding. The effect of the conductive MWNTs on the corrosion behavior of the composites was assessed using electrochemical impedance spectroscopy and potentiodynamic polarization curves. The in-plane and through-plane electrical conductivities of the molded plates were also determined. Scanning electron microscopy (SEM) analysis was used to observe the morphology of the composites. The corrosion mechanisms are discussed in connection with the morphological aspects revealed by the SEM micrographs. Furthermore, the influence of MWNTs on the thermal stability of the composites was investigated by thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials and composite preparation

A commercial ABS resin in powder form was supplied by Basf. Synthetic graphite (fuel cell grade) particles with purity ≥95.0%, surface area of 1.5 $m^2\ g^{-1}$ and typical size of 40 μm were supplied by Asbury Carbons. The multi-walled carbon nanotubes were purchased from Federal University of Minas Gerais (UFMG, Brazil), presenting a surface area of 300 $m^2\ g^{-1}$ and purity ≥90.0%.

All components of the composite bipolar plates were in powder form. Five different compositions were prepared as shown in Table 1. Initially, the components were mixed in a Turbula T10B powder blender for 30 min. The MWNTs did not receive any surface treatment prior to the preparation of the composite. Then, the mixture was compression molded in a hydraulic press at 250 °C and a pressure of 400 kg cm^{-2} for 10 min, forming discs with 30 mm diameter and 3 mm thickness. After water cooling, the molded disc was removed from the mold and characterized. These samples were employed for the through-plane electrical conductivity determination and for the electrochemical tests. The samples for the in-plane electrical conductivity determination were molded according to the same parameters, but with different dimensions (130 × 12.7 × 3 mm).

2.2. Characterization

The in-plane electrical conductivity was measured by means of the four point probe method, according to ASTM D4496. A programmable current source was applied through the outer two probes and the voltage drop across the two inner probes was measured with a precision voltmeter. The electrical conductivity (σ) was calculated according to equation (1), where i is the constant

Table 1
Compositions used in the preparation of the composite bipolar plates.

Specimen	Mass (%)		
	ABS	Synthetic graphite	MWNT
S0	15	85	0
S1	15	84	1
S2	15	83	2
S3	15	82	3
S4	15	81	4
S5	15	80	5