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SnO_2 nanocubes/bentonite modified SPEEK nanocomposite composite membrane for high performance and durable direct methanol fuel cells

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ABSTRACT

Tin oxide nanocubes/sulfonated bentonite (SnO_2/sBH) nanocomposite blended with acidified poly ether ether ketone (SPEEK) solid state electrolyte is developed for DMFCs. Morphological investigations reveal the existence of SnO_2 nanocubes on sheet-like structure of sBH and the uniform dispersion of above composite on SPEEK matrix. The layered sheet-like structure of BH act as heat diffusion barrier and the ceramic feature of SnO_2 further improves the thermal stability of a SPEEK membrane. The exposed large surface area of BH and tightly bound water molecules in SnO_2 and -SO_3H sites increase the water retention properties, which consequently enhance the ionic conductivity of SPEEK/sBH/SnO_2 composite membrane. Furthermore, the high aspect ratio of sBH and methanol resistive characteristic of SnO_2 lower the methanol diffusion channels in the sBH/SnO_2 composite membrane. With the coalition of above significant electrochemical properties, SPEEK/sBH/SnO_2 solid electrolyte demonstrates the high DMFC power density and excellent durability, which showers light on the viability of prepared membrane in high performance and durable DMFCs.

1. Introduction

DMFC is considered as the prodigious clean energy device for portable electronic devices [1–4], in which the solid state electrolyte administers a decisive role as an ion conductor and a methanol separator [5]. Commercially offered polymer electrolyte membrane in DMFC is Nafion, which demonstrates the elevated electrochemical performances along with the considerable physio-chemical stabilities [6]. However, the elevated methanol crossover of Nafion membrane ($\sim 10^{-6}$ cm^2 s^{-1}) at moderate temperature not only causes the fuel loss but also limits the overall cell voltage due to the mixed potential at cathode [7]. Furthermore, the tedious strategies involved in the synthesis process of Nafion increases their production cost and liberates the poisonous intermediates, restraining their applicability in fuel cells [8]. It directs the exploration of various cost-efficient and high performance polymeric membranes including sulfonated poly (ether sulfone)s (SPES), sulfonated poly(arylene ether sulfone) (SPAES), sulfonated polyimides (SPI), sulfonated polybenzimidazole (SPBI), and sulfonated poly(ether ether ketone) (SPEEK) [9,10]. Amid the above, the applicability of SPEEK membrane in DMFCs has garnered massive interest, owing to its good film forming ability, high thermal and mechanical stabilities, and easier processability. However, SPEEK membrane demonstrates the sufficient ionic conductivity only at the expense of high ion exchange capacity (IEC) values, leading to high swelling, deterioration in mechanical stability, and high fuel permeation [11]. Among the various strategies proposed to tackling the above constraints, SPEEK hybrid material with inorganic nanofillers generate the significant engrossment in DMFCs, owing to the benefits of proficient processing, high ionic conductivity, elevated mechanical and thermal stabilities, controlled swelling behavior, and high water retention properties [12,13]. It is due to the strong synergistic interaction between the extended interface created by the organic and inorganic components [14]. In response, numerous nanomaterials including inorganic metal oxide nanoparticles, bentonite (BH), carbon nanotubes (CNTs), and graphene oxide (GO) have been used as nanofillers for the modification of SPEEK membrane [15–17] to confining the methanol crossover paths with the acceleration of physical stabilities even under the high acidification of a host polymer. In specific, the exfoliated BH in polymeric matrices provides high fuel

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