



ORIGINAL ARTICLE

Tapioca binder for porous zinc anodes electrode in zinc–air batteries



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Abstract Tapioca was used as a binder for porous Zn anodes in an electrochemical zinc-air (Zn-air) battery system. The tapioca binder concentrations varied to find the optimum composition. The effect of the discharge rate at 100 mA on the constant current, current–potential and current density–power density of the Zn-air battery was measured and analyzed. At concentrations of 60–80 mg cm⁻³, the tapioca binder exhibited the optimum discharge capability, with a specific capacity of approximately 500 mA h g⁻¹ and a power density of 17 mW cm⁻². A morphological analysis proved that at this concentration, the binder is able to provide excellent binding between the Zn powders. Moreover, the structure of Zn as the active material was not affected by the addition of tapioca as the binder, as shown by the X-ray diffraction analysis. Furthermore, the conversion of Zn into ZnO represents the full utilization of the active material, which is a good indication that tapioca can be used as the binder.

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1. Introduction

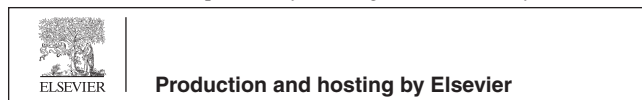
Tapioca is a common plant that can be found in almost every tropical country. Its biodegradable starch is an important source of carbohydrates (Atichokudomchai and Varavinit, 2003; Blagbrough et al., 2010; Breuninger et al., 2009). In general, the starch of tapioca is made up of two major macromolecular components, which can be identified as amylose and

amylopectin (Breuninger et al., 2009; Chung and Liu, 2009; Pérez et al., 2009). Amylose is a linear component polymer that is primarily composed of (1 → 4)-linked α -glucan (Fig. 1a). The degree of polymerization of this polymer can be as high as 600. In tapioca starch, the amylose content can vary from 17% to 20%. Alternatively, amylopectin is the major component of tapioca starch (Fig. 1b). This polymer is made up of $\alpha(1 \rightarrow 4)$ -linked α -glucan with an $\alpha(1 \rightarrow 6)$ branch point. Amylopectin is significantly different than amylose because amylopectin contains approximately 5% branch points (Chung and Liu, 2009; Pérez et al., 2009).

When tapioca starch is heated in excess water, an irreversible structure transition takes place, which is known as starch gelatinization or pasting. The granules of tapioca starch lose their birefringence and crystallinity as more water is absorbed. Upon cooling, tapioca starch experiences an increase in

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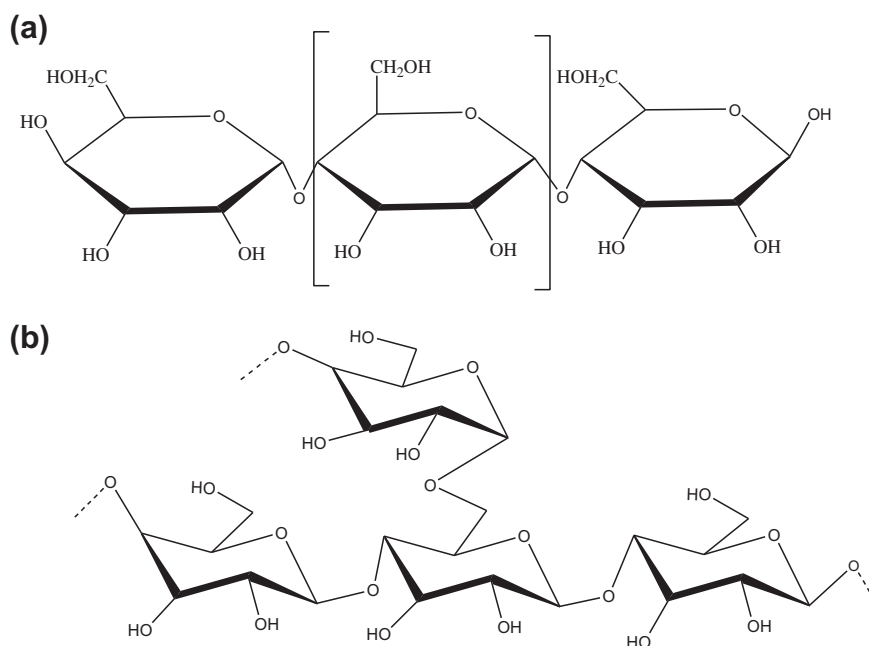


Figure 1 Molecular structure of the starch components (a) amylose and (b) amylopectin.

viscosity, and some loss of clarity can be seen before a weak gel or film is formed. The reassociation of the amylose molecules in the aqueous system is attributed to these changes. This gel-forming process is known as retrogradation (Biliaderis et al., 2009; Breuninger et al., 2009).

In recent advances in zinc-air (Zn-air) batteries, porous anodes made of powders of Zn have started to be utilized, rather than planar Zn anodes, which results in a higher effective surface area. Surface area is one of the major factors that governs anode mass utilization and thus affects the specific energy density produced from an electrochemical power source. A higher surface area per unit volume for a given amount of active material reduces the current density and leads to an increase in the electrode rate capability and active material utilization. To bind the powders of the active material and prevent them from disintegrating, various types of gels or binders have been used, such as polytetrafluoroethylene (Lee et al., 2006; Müller et al., 1998), Carbopol gel (Yang and Lin, 2002; Wu et al., 2006) and sago (Masri and Mohamad, 2009).

Because tapioca can be dissolved in water without any additional materials that could degrade the properties of pure Zn, it is suitable for producing a porous anode. To the best of our knowledge, detailed studies concerning the application of tapioca starch as a binder for porous Zn anodes have yet to be reported. Thus, the aim of this work was to fabricate an electrochemical Zn-air battery by employing tapioca as the binder for the porous Zn anode and to determine the optimum composition of the tapioca binder. Morphological and phase identification studies of the porous anode were used to support the findings.

2. Experimental

2.1. Preparation of the tapioca binder and porous zinc anode

Tapioca powder (THC Sdn. Bhd., Penang) (1.5, 2.0, 2.5 and 3.0 g) was mixed with 25 ml of deionized water and stirred

for 10 min. Then, 3.0 ml of 0.1 M hydrochloric acid was added to the solution, and it was stirred for another 10 min. Next, 2.0 ml of glycerol was added to the solution, which was stirred and heated at 90 °C until a clear solution was obtained. In this state, the acidity of the mixture was balanced with sodium hydroxide. Lastly, 4 ml of the 60, 80, 100 and 120 mg cm⁻³ mixture was mixed with 4 g of zinc powder (Zn, Merck) and gelatinized at room temperature. The weight ratio of Zn and binder was 1:1. Then, the anode paste was cast onto a nickel-plated mesh that had been snugly fitted to a plastic casing and then dried at room temperature. The porous Zn anode was stored in a dry cabinet prior to being evaluated.

2.2. Fabrication and characterization of the zinc-air battery

The sago gel electrolyte used in the current work was composed of 6 M KOH (KOH, Merck) and sago powder. The sago gel solution was prepared by dissolving 2.0 g of natural sago with 6 M KOH solutions. Details of the preparation of the sago gel electrolyte were reported elsewhere (Masri et al., 2010; Jamaludin et al., 2010).

The air-cathode electrode was purchased from MEET Co., Ltd, Korea. The details of the fabrication of the battery were reported in a previous article (Masri and Mohamad, 2009, 2013). The electrochemical characterizations of the Zn-air batteries were performed at a constant current of 100 mA (or 7.9 mA cm⁻² with respect to the Zn anode area) at room temperature using an ARBIN Instrument BT2000 Battery Testing System.

2.3. Characterizations of the porous anodes

The porous Zn anodes were characterized using a field-emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). The FESEM micrographs were recorded using a Zeiss SUPRA 35 VP, and the XRD measurements were taken using a Bruker AXS D9.

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