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Electrochemical properties of a low molecular weight gel electrolyte for nickel/metal hydride cell



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ABSTRACT

A low molecular weight gel electrolyte was formed by the self-assembly of a low molecular weight gelator in aqueous solution electrolyte and used in a Ni/MH cell. When the temperature was below 348 K, the low molecular weight gel electrolyte was used as a solid. The high ionic conductivity $(1.51 \times 10^{-2} S cm^{-1})$ and a stable electro- chemical window of the gel electrolyte were confirmed at 303 K. A Ni/MH cell was fabricated with the low molecular weight gel electrolyte, and its charge-discharge and capacity retention characteristics were measured. The deflection of the cell with gel electrolyte was smaller than that of the cell with aqueous solution electrolyte. Therefore, the gel electrolyte had good electrochemical properties while solving the problem of solution leakage.

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1. Introduction

Gel electrolytes have been extensively studied in the past few decades for their applications to lithium batteries [1,2], lithium/sulfur batteries [3] and dye-sensitive solar cells [4]. Indeed, gel electrolytes present some advantages in comparsion with conventional liquid electrolytes, such as: high safety, good mechanical strength, low convection, long cycle life and so on [5–7].

Gel electrolytes can be classified into polymer gel electrolytes and low molecular weight gel electrolytes according to the gelators. Nickel/metal hydride (Ni/MH) cells with polymer gel electrolytes are investigated in recent years. Yang reported a Ni/MH cell based on a poly(vinyl alcohol)-poly(ethylene oxide)-KOH electrolyte [8]. Iwakura investigated Ni/MH cells based on alkaline polymer gel electrolytes and tested their charge-discharge and capacity retention characteristics [9]. Palacios prepared a series of alkaline solid electrolyte membranes, based on poly(vinyl alcohol), potassium hydroxide and water, and the ionic conductivity of the membranes were about $2.3 \times 10^{-3} S cm^{-1}$ at room temperature [10].

However, low molecular weight gel electrolytes with high ionic conductivities for use in the Ni/MH cells have not been reported. Unlike the polymer electrolytes mentioned above, low molecular weight gel electrolytes based on low molecular weight gelators were formed by self-assembly of the gelators at low temperature through intermolecular forces such as hydrogen bonding, π - π interactions and Van der Waals force [11–14]. This process is reversible; that is, the low molecular weight gel electrolyte can melt again at high temperature and be reformed under cooling. Because of the reversibility, the preparation of the Ni/MH cell is much easier than that of the cell with polymer electrolyte. Several groups have investigated organogel electrolytes [15] and ionic liquid gel electrolytes [16–18]. In addition, we also succeed in the assembly of supercapacitors [19] and quasi-solid-state dye-sensitized solar cells [20] with low molecular weight gel electrolytes.

In this work, gel electrolyte was prepared using 2,4-(m-methylbenzylidene) -D- sorbitol (m-MBS) (Scheme 1) as the gelator. The Ni/MH cells were prepared using the gel electrolyte and aqueous solution electrolyte, respectively, and their charge- discharge and charge retention characteristics were measured and compared.

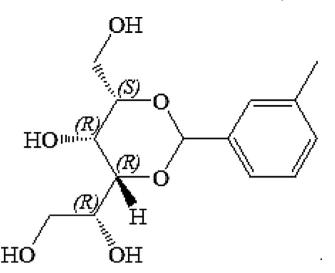
2. Experimental

2.1. Synthesis of m-MBS

The gelator, *m*-MBS was prepared according to the method described previously [21]. To a solution of D-sorbitol (10 g, 0.055 *mol*) in water (14 *mL*), *m*-methyl- benzaldehyde (6 g, 0.05 *mol*) and concentrated HCl (2 *mL*) were added at 288 *K*. The resulting mixture was stirred for 4 *h* at room temperature during which a product precipitated. The precipitate was filtered and the filter cake was washed with water (50 *mL*) and ethyl acetate (50 *mL*). The filter cake was suspended in water (150 *mL*) containing



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Scheme 1. Chemical structure of the gelator, 2,4-(*m*-methyl-benzylidene)-D-sorbitol (*m*-MBS).

 Na_2CO_3 (2 g) and heated at 398 K for 3 h. After filtration while hot, the filtrate was kept at 298 K for 3 h and the crystalline solid thus generated was collected by filtration.

2.2. Preparation and characterization of the gel electrolyte

The gelator and aqueous solution electrolyte (6M KOH and 1M LiOH) were heated in a glass tube until the gelator completely dissolved. After cooling to room temperature, the gel electrolyte was obtained. The minimum amount of gelator required is defined as the minimum gelation concentration (MGC) [22].

The gel-to-sol phase transition temperature (T_{gel}) of the gel electrolyte was determined by the ball-drop method [23]. A small steel ball (0.88 g) was placed on the top of the gel in a test tube (Φ 12 × 120 mm). The tube was then slowly heated (1 K min⁻¹) in a thermostatic oil bath. When the ball fell to the bottom of the tube, the temperature was recorded as the gel-to-sol phase transition temperature (T_{gel}).

2.3. Electrochemical behavior

The low molecular weight gel electrolyte used for electrochemical measurement was prepared with 0.5 *wt% m*-MBS.

The low molecular weight gel electrolyte was placed in a conventional three-electrode cell with a mercuric oxide reference electrode (mercury-mercuric oxide electrode) and a Pt plate as the counter electrode. The working electrode was a 3 mm glassy carbon (GC) disk insulated in a 7 mm diameter Teflon rod. Cyclic voltammograms of the electrolyte were measured using a Zhanner IM6e electrochemical working station under N₂ atmosphere at a scanning rate of 80 mV s⁻¹. The experiments were conducted at $298 \pm 1 K$.

The ionic conductivity of the electrolytes was measured with a DDS-12B conductivity meter. The tested electrode was inserted into the gel electrolyte before the formation of the gel.

The negative electrode was prepared by pasting and thermopressing a mixture of the MH powder, nickel powder and PTFE (60 *wt%* PTFE dispersion) in weight ratio of MH: Ni: PTFE =84.5: 0.5: 15 on Ni foam under 11 *MPa*. And the positive electrode was prepared by pressing a mixture of the Ni(OH)₂ powder, CoO powder and PTFE (60 *wt%* PTFE dispersion) in weight ratio of Ni(OH)₂: CoO: PTFE =80: 5: 15 on a Ni foam under 11 *MPa*. The thickness of the negative electrode and positive electrode were 0.3 *mm* and 0.4 *mm* respectively. The Ni-MH experimental cell was wrapped with a PP

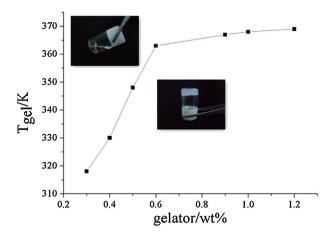


Fig. 1. T_{gel} of the gel electrolyte as a function of gelator concentration.

fiber felt separator. After winding the three-layer structure of the negative electrode/electrolyte/positive, electrode formed a cylinder. And the cylinder was set in a cell holder. The electrolyte was injected at 348 K by many times when the gel electrolyte was liquid. The cells with 6000 *mAh* nominal capacity were fabricated with low molecular weight gel electrolyte and aqueous solution electrolyte.

In the charge-discharge test, the Ni-MH cells were charged for 10 h at the rate of C/10, 30 min rest period, and discharged at the rate of C/5 to 1.0 V. The deflections of the Ni-MH cells were tested by the lossness deformation determinator of the Ni/MH at C/2 and C/3, respectively [24].

In the charge-discharge cycle life tests, fifty cycles was defined as a period. First the cell was charged at C/10 for 16 *h* and discharge at C/3 for 136 *min* in the first cycle. Then the cell was charged at C/3 for 3 *h* and discharge at C/3 for 136 *min* in the second to the forth cycle. In the fifth cycle, the cell was charged at C/3 for 3 *h* and discharge at C/3 to 1.0 *V*. In the sixth to the forty eighth cycles, the cell was tested as the first to the firth cycle. The next forty ninth cycle, the cell was charged at C/3 for 3 *h* and discharged at C/3 to 1.0 *V*. In the fiftieth cycle, the cell was charged at C/3 for 3.5 *h*, 1 *h* rest period, and discharged at C/3 to 1.0 *V*. We recorded the discharge capacity of the fiftieth cycle in each period.

3. Results and discussion

3.1. Thermodynamic stability of the gel electrolytes

Fig. 1 The T_{gel} characterizes the dissociation temperature of gelator aggregation. The T_{gel} of the gel electrolyte with different gelator concentration is shown in Fig. 1. When the amount of gelator is greater than 0.5 *wt%*, the T_{gel} values are above 348 K. In addition, the T_{gel} increased with increasing gelator concentration. The T_{gel} of the electrolyte is much higher than some other gel electrolyte formed by low molecular weight gelators [15]. As a consequence, the gel electrolyte is heated.

3.2. Ionic conductivity of the electrolytes

The change in the ionic conductivity of the electrolytes as a function of the gelator concentration is shown in Fig. 2. A high ionic conductivity $(1.51 \times 10^{-2} S cm^{-1})$ for the gel electrolyte at 303 K is observed when the amount of the gelator is 0.5 *wt%*, which is higher than some polymer gel electrolyte [10,25]. As shown in Fig. 2, gelation has only a little influence on the ionic conductivity. The conductivities of the gels are slightly lower than those of pure solution electrolyte. The differences of ionic conductivity between gels

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