Research Article

Improved Composite Gel Electrolyte by Layered Vermiculite for Quasi-Solid-State Dye-Sensitized Solar Cells

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A composite quasisolid electrolyte is prepared by adding a layered vermiculite (VMT) into the iodide/triiodide electrolyte including 4-tert-butylpyridine, which obviously improves the photovoltaic properties of quasisolid dye-sensitized solar cells (DSSCs). When adding 6 wt% VMT, the maximum photovoltaic conversion efficiency of 3.89% is obtained, which reaches more than two times greater than that without VMT. This enhancement effect is primarily explained by studying the Nyquist spectra, dark currents, and photovoltaic conversion efficiency.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted an ever-increasing attention since reported by O'Regan and Grätzel in 1991 [1] for its low-cost, environmental friendliness, and potential high conversion efficiency, which was considered to be a strong contender of the next-generation solar cells in the near future. Generally, a mainstream DSSC is composed of three main parts: a dye-adsorbed porous nanocrystalline TiO_2 film supported on a transparent conducting glass as the photoanode, an organic liquid electrolyte, essentially containing an iodide/triiodide redox couple, and a platinized transparent glass substrate as the counter electrode. These three layers are sandwiched together. Electrolytes play an important role in the DSSCs as the charge exchange medium. The organic liquid electrolyte was commonly used in traditional DSSCs, which is associated with problems such as hermetic sealing of the cell, solvent volatilization and leakage, bad long-term stability, decomposing dye, and corroding Pt electrode.

Recently, many efforts have been made to overcome the above problems of traditional DSSCs with liquid electrolytes, and solid-state and quasi-solid-state DSSCs have been intensely studied with various approaches. Some novel technologies and materials including p-type semiconductors [2], organic and inorganic holes conductors [3], and polymer gel electrolytes [4, 5] were used in new electrolytes to improve properties. Among them, polymer based quasi-solid-state electrolytes are a very good choice for its high ionic conductivity, long-term stability, good interfacial filling properties, and inhibiting leakage, which commonly have a polymer and ionic liquid electrolytes containing dispersed nanocomponents. Some ceramic nanoparticles such as SiO_2 [6], TiC [7] and TiN [8] were added into ionic liquids-based electrolytes for DSSCs, and an enhanced conversion efficiency was obtained. In our previous work [9, 10], some layered materials such as α-zirconium phosphate and Mg-Al hydrotalcite were added into the iodide/triiodide ionic liquid to prepare quasi-solid-state electrolytes, which obviously improves the photovoltaic properties of quasisolid DSSCs. Vermiculite (VMT) is not only a layered mica-type silicate but is also with a large surface area and strong absorptive capacity and has often been studied for the preparation of composites [11, 12]. In this paper, a new composite gel polymer electrolyte was prepared by adding vermiculite (VMT) powder into iodide-based liquid electrolyte with the addition of 4-tert-butylpyridine (TBP), propylene carbonate (PC), and poly (ethylene oxide) (PEO-600,000).
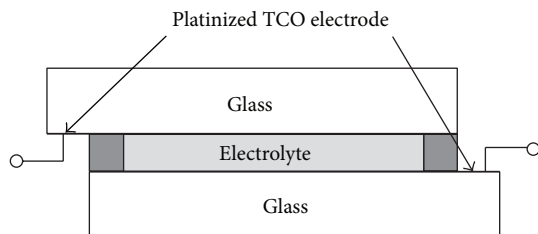
FIGURE 1: Schematic diagram of the experimental thin-layer cell configuration employed for the electrochemical measurements.

The electrochemical properties of the composite electrolyte were analyzed systematically by testing Nyquist diagram, and a typical DSSC was packaged with the new quasi-solid-state composite electrolyte to measure photovoltaic properties.

2. Experimental

2.1. Preparation of VMT and Composite Gel Polymer Electrolyte. The starting VMT was supplied by Bright Mining Co. (Shanghai, China). After VMT was ball-milled for 6 h in the solvent of deionized water, the ultrasonic irradiation method reported by Nguyen et al. [13] was used to prepare the layered vermiculite (VMT) powders.

Then, VMT powders with the contents of 0 wt%, 3 wt%, 6 wt%, 9 wt%, and 12 wt%, relative to the weight of TBP, were added to the iodide-based gel polymer electrolyte prepared according to [14], which contained 0.5 M LiI, 0.05 M I_2, 6 mL PC, 0.5 M TBP, 0.4 g PEO-600,000, and acetonitrile solvent. After stirring strongly for 72 h at 80°C, the composite gel polymer electrolytes including layered VMT were obtained.

2.2. Testing Device and Characterization Method. X-ray diffraction (XRD Rigaku D/max-RB) with CuKa radiation was used for phase analysis of the powders under 40 kV and 30 mA. Scanning electron microscopy (SEM, INSPECTF FEI, Netherlands) was used to observe the micrographs. Simple thin-layer cells were manufactured to measure AC impedance according to [15]. The cell was made up of two identical platinized TCO-coated glass substrates separated by Surlyn thermal packaging adhesive and filled with the composite electrolyte with VMT additives, as shown in Figure 1. The active area of the electrodes was about 0.16 cm^2 and the distance between the electrodes was about 25 μm. Electrochemical impedance spectra (EIS) were obtained by using CHI660c electrochemical analyzer (CH Instrument Co., ltd. China). Sinusoidal perturbations of 10 mV at frequencies from 0.01 Hz to 100 kHz with zero bias potential were applied on thin-layer cells with a two-electrode mode as shown in Figure 1. In order to study the photovoltaic properties of the DSSCs with the composite electrolytes containing VMT, quasisolid DSSCs were packaged according to the previous published procedures [9, 10] from dye-coated TiO$_2$ film photoanodes, counterelectrodes (500 nm thick, Pt), and composite gel polymer electrolytes containing VMT. Photovoltaic properties were measured at 100 mW cm^{-2} light intensity under AM 1.5 irradiation of xenon lamp, while the
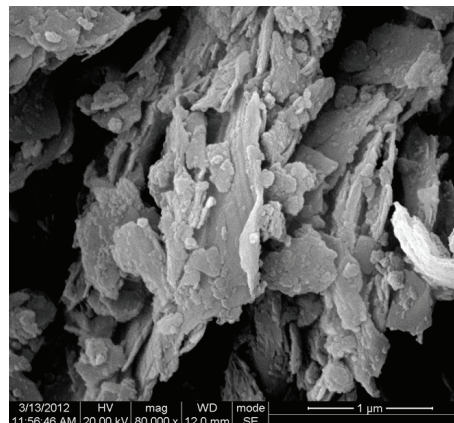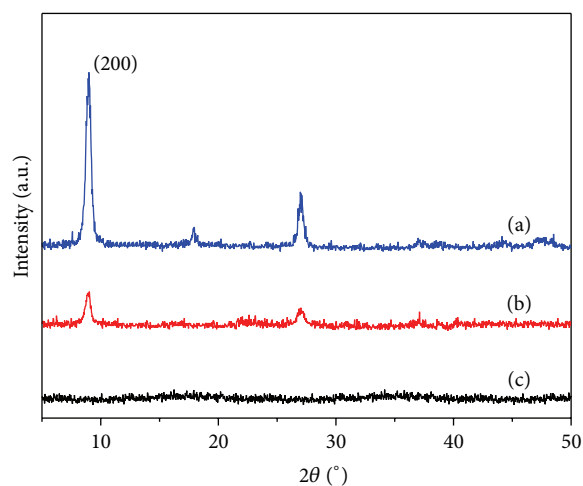

FIGURE 2: SEM micrograph of VMT powder.

FIGURE 3: X-ray diffraction patterns of (a) VMT powder, (b) the composite electrolyte membrane with 6 wt% VMT, (c) the composite electrolyte membrane with 0 wt% VMT.

dark current density is measured in dark. All measurements were carried out at room temperature.

3. Results and Discussion

3.1. Analysis of VMT Powders. Figure 2 shows a SEM micrograph of VMT powders, and the layered structure with a nanoscale layer thickness can be observed. X-ray diffraction patterns of the prepared VMT powder and composite electrolytes are shown in Figure 3. As shown in Figure 3(a), the prepared VMT powders are well-crystallized with the strongest diffraction peaks at 8.96°, indexed as (200) peak [13]. After 6 wt% VMT additive was mixed into iodine-based PEO electrolyte and coated on the photoanode thin film, the (200) peak was still detected in the obtained electrolyte membrane as shown in Figure 3(b).

3.2. The Influence of VMT on the Conductivity. The Nyquist spectra of thin-layer cells with composite gel iodide-based electrolytes containing different contents of VMT are shown
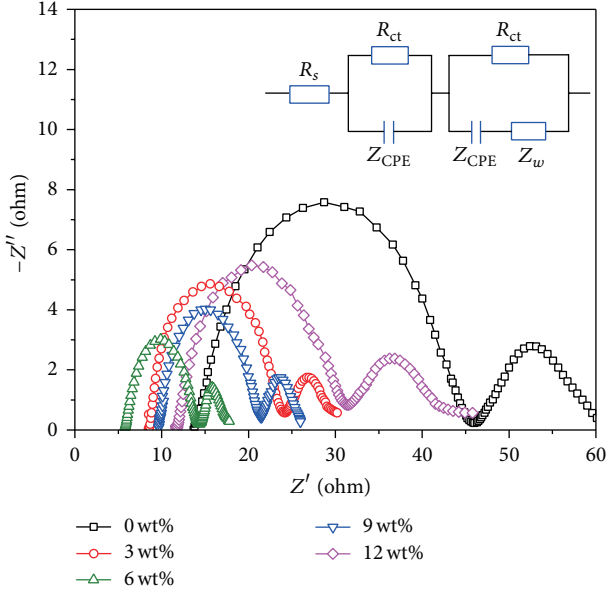
FIGURE 4: Nyquist diagram of thin-layer cells with various contents of VMT and the inset shows the equivalent circuit.

TABLE 1: The results for the R_{ct} and corresponding σ of the iodide-based gel electrolytes with various contents of VMT.

VMT (wt%)	R_{ct} (Ω)	R_s (Ω)	σ (10^{-4} S cm^{-1})
0	32.04	13.69	11.41
3	15.05	9.11	17.15
6	8.35	5.75	27.17
9	13.47	7.85	19.91
12	19.64	11.63	13.44

in Figure 4. The equivalent circuit is shown as the inset of Figure 4. Each curve is composed of two semicircles. The one in the high frequency region represents the charge transfer resistance (R_{ct}) of Pt/electrolyte interface, and the other one in the low frequency region relates to the Warburg impedance (Z_w) [8]. R_s is the ohmic serial resistance and Z_{CPE} is the impedance of electrical double layer. Based on the equivalent circuit, the fitting data of the charge transfer resistance (R_{ct}) and the ohmic serial resistance (R_s) were obtained. Then the ion conductivity of the electrolyte (σ) can be obtained from the equation $\sigma = l/(R_s a)$ [4], where a are l are the active area of the electrodes (here $a = 0.16$ cm^2) and the distance between electrodes (here $l = 0.25$ μm), respectively. The results for the R_{ct} values and R_s values and corresponding σ values of iodide-based gel electrolytes with various contents of VMT are summarized in Table 1.

As shown in Figure 4 and Table 1, the R_{ct} values and the R_s values of the cells decrease markedly and the corresponding σ values increase with adding VMT up to 6 wt%. Here, VMT as dispersed second phase insulating particles affected drastically the conductivities of composite iodide-based gel electrolytes. Quite a few works [16, 17] reported the effect of dispersed second phase particles on the ionic

TABLE 2: The photovoltaic parameters of the DSSCs with various contents of VMT.

VMT (wt%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
0	5.08	0.62	0.54	1.70
3	9.07	0.64	0.53	3.07
6	9.77	0.67	0.59	3.89
9	8.53	0.66	0.55	3.10
12	7.15	0.64	0.53	2.43

conduction. When adding the insulating phase in the ion-conductive phase, ionic conductivity will first increase and then decrease. Nan developed an improved and simple self-consistent effective-medium theory to explain the effect [18]. It has now become widely accepted that the enhancement effect of conductivity is related to creating highly conductive paths along the interfaces between the electrolyte matrix and the second phase grains [18]. The highly conductive paths can be an interfacial layer with high concentrations of defects, a space charge layer, and/or an absorbed water layer. VMT has a layered structure with a large surface area, which means there is enough interface to create conductive paths. When the content of VMT is 6 wt%, the minimum R_{ct} value of 8.35 Ω and the minimum R_s value of 5.75 Ω are obtained, corresponding with the maximum σ value of 27.17 $*$ 10^{-4} S cm^{-1}. While the content of VMT is over 6 wt%, the inert second phase particles directly contact each other to form continuum percolation net clusters, which tends to limit ion movement and decrease the conductivity [17, 18], and, as a result, the R_{ct} values and the R_s value increase and the σ values decrease markedly.

3.3. The Influence of VMT on the Photovoltaic Conversion Efficiency. Figure 5(a) is the J-V curves of thin-layer cells with various VMT contents. The results for short-circuit current density (J_{sc}), open circuit potential (V_{oc}), fill factor (FF), and conversion efficiency (η) of the DSSCs with different additions of VMT are summarized in Table 2. The DSSCs with the electrolytes adding VMT show a higher open circuit potential (V_{oc}) and significantly higher short current density (J_{sc}) than that without adding VMT. V_{oc} and J_{sc} increase first and then decrease with the increase of VMT contents. In order to study the influence of electrolytes with adding various contents of VMT on the above photoelectric properties, the dark current density-voltage curves of the DSSCs with various contents of VMT are shown in Figure 5(b). It can be easily found that the dark current density decreases when adding the VMT. As the content of VMT increases to 6 wt%, the dark current density of the DSSC is suppressed to a minimum and increases quickly as the content of VMT further increases over 6 wt% to 12 wt%.

The change in both V_{oc} and J_{sc} of the DSSCs is related to the dark current density. The enhanced V_{oc} is due to the suppression of the dark current in the TiO$_2$/electrolyte interface. The fact that the onset of the dark current of DSSCs occurs at the higher forward bias indicates the lower I_3^- reduction rate (k_{et}) [9, 19]. The decrease of I_3^- reduction rate
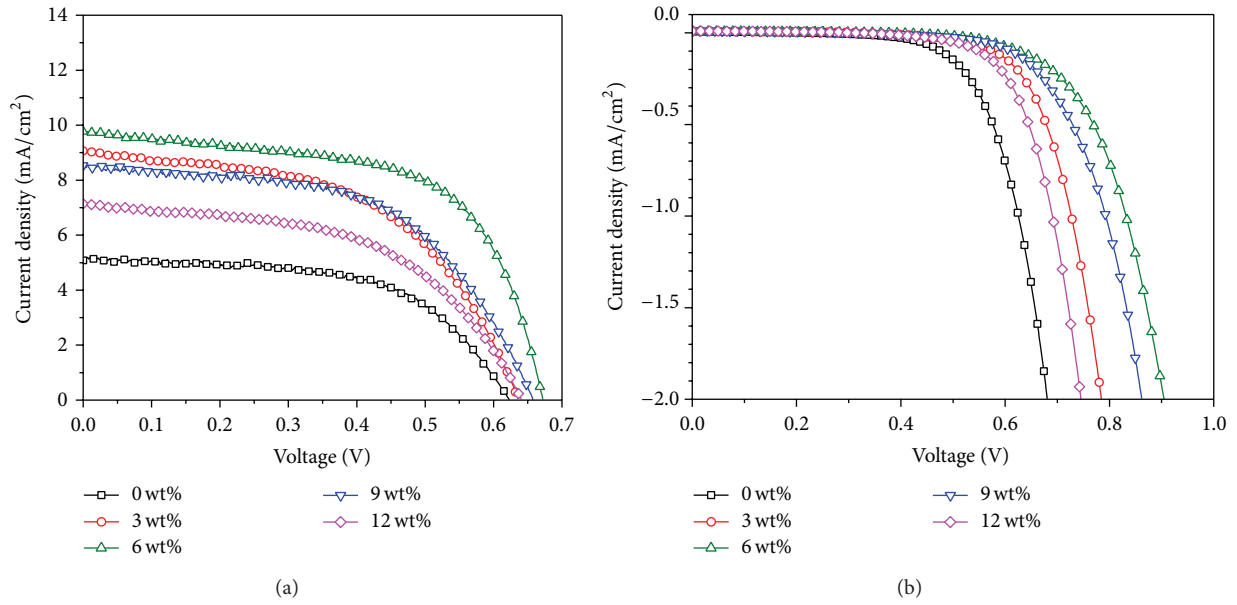
(a)

(b)

FIGURE 5: The J-V curves of DSSCs with composite electrolytes containing various contents of VMT (a) under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2}; (b) in the dark.

will lead to an increase of V_{oc} according to the following equation [19]:

$$V_{oc} = \frac{kT}{e} \ln \left(\frac{I_{inj}}{n_{cb} k_{et} \left[I_3^- \right]} \right), \tag{1}$$

where I_{inj}, n_{cb}, and k_{et} are the flux of charge originating from sensitized injection related to the electron back transfer rate, the concentration of electrons at the TiO$_2$ surface, and the rate constants for I_3^- reduction, respectively. As shown in Figure 5(b), the onset of the dark current of DSSCs occurs at 227, 335, 378, 325, and 319 mV with various electrolytes adding 0 wt%, 3 wt%, 6 wt%, 9 wt%, and 12 wt% of VMT, respectively. The higher onset voltage value of the dark current of DSSCs with adding VMT than that without adding VMT reveals that VMT can efficiently suppress the dark reaction to obtain higher V_{oc}. On the other hand, the J_{sc} of DSSCs is also associated with the dark current, which can be given by the equation $J_{sc} = I_{inj} - J_{rec}$, where I_{inj} and J_{rec} are the electron injection current density and the recombination current density, respectively [20]. The electron injection current density should be constant since all the DSSCs have the same electrodes and experimental conditions. The recombination current mainly manifests as the dark current, so the recombination current density has similar variation trend with the dark current density [21]. Consequently J_{sc} increases with the decrease of the dark current density. As a consequence, proper addition of VMT can improve both J_{sc} and V_{oc} of the DSSC, and the best ratio is about 6 wt% of VMT. When the content of VMT is 6 wt%, the conversion efficiency (η) is up to the maximum of 3.89%, which is more than two times greater than that without

adding VMT. While the content of VMT is over 6 wt%, the conversion efficiency (η) decreases quickly.

4. Conclusions

In summary, we prepared a quasi-solid-state composite electrolyte by adding layered vermiculite (VMT) powder into the iodide-based electrolyte including PC, TBP, and PEO-600,000. Electrochemical analysis was done on the DSSCs with various electrolytes adding different contents of VMT. The results showed that VMT as a dispersed second phase insulating particles affected drastically the conductivities of composite electrolytes. The reduction of the dark current density with adding VMT indicated that the J_{sc} and V_{oc} increased with the addition of appropriate amount of VMT, compared to DSSCs without VMT. When the content of VMT reached 6 wt%, the conversion efficiency (η) was maximized to 3.89%, which was more than two times greater than that without addition of the VMT.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
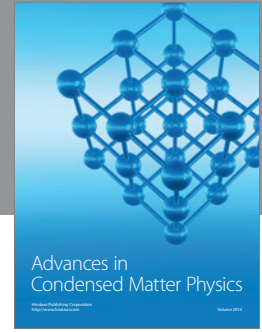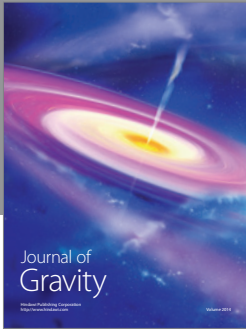
Acknowledgments

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