

Cheap and Environmentally Benign Electrochemical Energy Storage and Conversion Devices Based on AlI₃ Electrolytes

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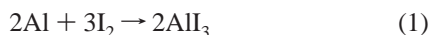
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Cheap and environmentally benign electrochemical energy conversion and storage devices, including primary and secondary batteries, dye-sensitized solar cells (DSSCs), supercapacitors, fuel cells, and so on, are in great demand for all kinds of electronic devices.¹ The finding of new electrolytes always plays a key role for their technical progress.² Here we report a new Al/I₂ primary battery system. Different than the operating mechanism in other Al-based batteries, in which an Al electrode is active and dissolved into aqueous or nonaqueous liquid electrolytes,³ AlI₃ is formed spontaneously in the Al/I₂ battery when an aluminum electrode and an iodine electrode are brought into contact at room temperature. Then I⁻ anions transport across the AlI₃ solid electrolyte for further reactions. On the other hand, it is found that an AlI₃-ethanol electrolyte can be prepared simply by adding aluminum powder and iodine into ethanol at ambient conditions. A DSSC using this AlI₃-ethanol electrolyte achieved an energy conversion efficiency of 5.9% at AM 1.5 (100 mW/cm⁻²). This is comparable to the DSSC using a LiI-nitrile electrolyte, where expensive anhydrous LiI and poisonous acetonitrile or methoxypropionitrile are used and the electrolytes are prepared under dry conditions.

An Al/I₂ cell was constructed as follows. An Al plate with a thickness of 0.5 mm was used as an anode directly. Iodine and graphite with a weight ratio of 8:2 were mixed mechanically and pressed into a pellet (diameter = 11.3 mm, thickness = 0.5 mm) as a cathode. Then both electrodes were put into a two-electrode Teflon-lined cell using stainless steel plates as current collectors. The cells were assembled and measured in an Ar-filled glovebox. No separator or electrolyte was used in this case.

A typical discharging curve of the Al/I₂ cell is given in Figure 1. The discharging voltage starts at 0.79 V and decreases gradually. The electrochemical reaction could be written as



According to the Nernst equation ($\Delta_r G = -nEF$), the thermodynamic equilibrium voltage (noted as E) of this reaction is 0.962 V. The large difference between E and the working voltage as well as the decreasing voltage upon discharging depth indicates that a high internal polarization exists and increases gradually in this cell. This agrees well with the reaction model that an ionic conductive electrolyte film is growing gradually sandwiched between Al and I₂ electrodes during the electrochemical reaction of aluminum and iodine.

AlI₃ could be prepared by heating aluminum and iodine powder at 300 °C for 24 h.⁴ It is confirmed here that AlI₃ can be formed

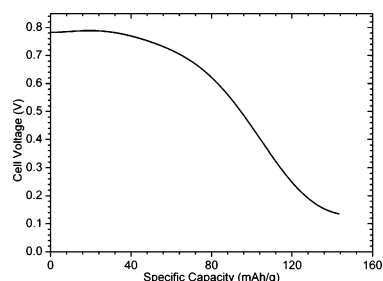


Figure 1. Discharge behavior of an Al/I₂ cell at a rate of 0.5 C (5 mA/cm²).

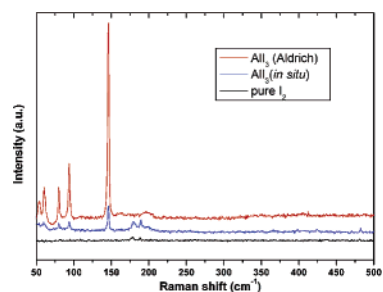


Figure 2. The Raman shifts of iodine (black line), commercial aluminum iodide (red line), and a mixture of aluminum powder and iodine (blue line).

even when aluminum powder was mixed with iodine powder mechanically at room temperature (evidenced by Raman spectra, Figure 2). Obviously, the reaction mechanism of the Al/I₂ cell can be described as a thin AlI₃ electrolyte layer formed once the Al anode and I₂ cathode are in contact. The consequent electrochemical reaction is related to the diffusion of either Al³⁺ ions or I⁻ ions across the AlI₃ layer.

To clarify the transport mechanism, an iodide ion conductor, LiI-(3-hydroxypropionitrile)₄ (LiI(HPN)₄) with 15 wt % SiO₂ (15 nm), was used as a solid electrolyte sandwiched between Al and I₂ electrodes to assemble an Al/LiI(HPN)₄-15 wt % SiO₂/I₂ cell. This solid electrolyte shows a mono-ion (I⁻) transport feature with an ion conductivity of 1.3 × 10⁻³ S/cm at room temperature.⁵ The discharge curve of the Al/LiI(HPN)₄-15 wt % SiO₂/I₂ cell is shown in Figure 3. It works well even when the cell is discharged at the current density of 5 mA/cm². Apparently, the initial polarization loss in the Al/LiI(HPN)₄ + 15 wt % SiO₂/I₂ cell is higher than that in the Al/I₂-C cell due to the addition of LiI(HPN)₄ + 15 wt % SiO₂ electrolyte. This result strongly supports that the operation of the Al/LiI(HPN)₄-15 wt % SiO₂/I₂ cell is based on the transport of I⁻ ions. Thus, the Al/I₂ cell is demonstrated as an iodide ion primary battery. Compared with the Li/I₂ battery, which is normally operated below 0.1 mA/cm²,⁶ the Al/I₂ cell can supply a large

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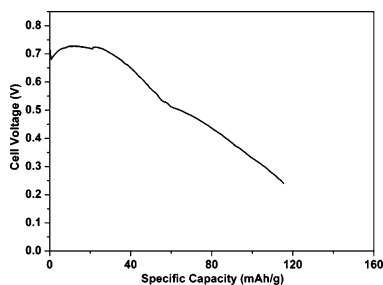


Figure 3. Discharge behavior of Al/LiI(HPN)₄ + 15 wt % SiO₂/I₂ cell at the discharge rate of 0.5 C (5 mA/cm²).

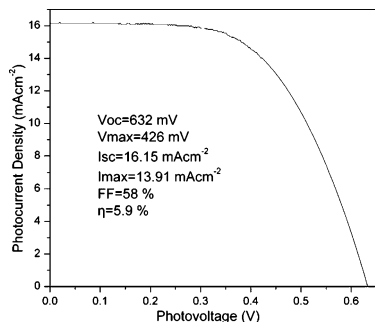


Figure 4. The photocurrent–voltage characteristics of a DSSC using the aluminum iodide electrolyte A in ethanol ($[I^-] = 0.3$ M, $[I_2] = 0.03$ M, ethanol/TBP = 8:1 (v/v), measured under AM 1.5, 100 mW/cm²).

discharge rate with discharge current density at an order of mA/cm² (see Figure S1). This should be related to fast transport of I⁻ ions in the AlI₃ electrolyte at room temperature, needing further investigation. The low cost of the Al/I₂ system as well as the feature of environmental friendliness makes this system as an attractive primary battery.

The AlI₃–ethanol electrolyte was prepared as follows. Excess aluminum powder and iodine (A.R.) were added into ethanol and stirred for about 2–5 h at ambient conditions. A clear and colorless solution could be obtained after filtering out excess aluminum powder. In this way, AlI₃ was formed and existed in ethanol as Al³⁺ and I⁻ (see Supporting Information). Then, appropriate amounts of 4-*tert*-butylpyridine (TBP) and iodine were added into the solution to form the final electrolyte (A). For comparison, two similar electrolytes were also prepared by dissolving the commercial reagents of aluminum iodide (Aldrich, 95%) and lithium iodide (Aldrich, 99.9%) directly in ethanol. TBP and iodine were also included in the above electrolytes (B and C, respectively). In all cases, the concentration of I⁻ was kept at 0.3 M.

By optimizing all of the components of DSSC (see Supporting Information, Figures S2 and S3), a high energy conversion efficiency (η) of 5.9% was achieved using AlI₃-based electrolyte A. Figure 4 shows the photocurrent–voltage (I – V) characteristic of the DSSC using electrolyte A. The corresponding parameters have an open-circuit voltage (V_{oc}) of 632 mV, a short-circuit photocurrent density (I_{sc}) of 16.15 mA/cm², and a fill factor (FF) of 0.58. This efficiency is higher than the DSSC using the LiI–ethanol-based electrolyte we reported before,⁷ due to the enhanced ionic conductivities (see Supporting Information). It also should be mentioned that the performance of DSSC using the AlI₃ electrolyte A prepared in situ is better than the DSSC using the

AlI₃ electrolyte B (commercial AlI₃ reagent dissolved into ethanol) and electrolyte C (see Supporting Information Figure S3).

For comparison, a traditional electrolyte was also prepared, the composition of which was 0.6 M dimethylpropylimidazolium iodide, 0.1 M of lithium iodide, 0.5 M TBP, and 0.1 M of iodine in methoxypropionitrile (MPN).⁸ A DSSC using the traditional electrolyte achieved an efficiency of 7.2% with $V_{oc} = 665$ mV, $I_{sc} = 16.87$ mA/cm², and FF = 0.64. The difference between the reported best result ($\eta = 10.4\%$)⁸ and our efficiency for the same system indicates that other components except the electrolyte are not well optimized. Thus, we are convinced that the efficiency of DSSC using the aluminum iodide-based electrolyte can be further improved by optimizing the TiO₂ film, other components, and assembling procedures of DSSC.

Above preliminary results of DSSC using the AlI₃–ethanol electrolyte system shows a promising future for achieving high energy conversion efficiencies with the advantages of low cost and environmental benignity.

In summary, we report cheap, environmentally benign energy conversion and storage devices, that is, an Al/I₂ primary battery and a DSSC based on AlI₃ electrolyte. It is believed that this AlI₃ electrolyte, based on iodide transport, can find other applications.

Acknowledgment. The authors appreciate the financial support from the National “863” and “973” Programs and the “100-talent” project of CAS.

Supporting Information Available: Al/I₂ battery discharged at different rates, the procedure of TiO₂ film preparation and cell fabrication, the optimization of the concentration of TBP and iodine in the electrolytes, experiments for determining the dissociated state of AlI₃ in ethanol by UV–vis spectra, FT-Raman spectra, conductivity measurements of AlI₃ and LiI solutions, secondary ion mass spectrometry (Cs⁺ ion being the incident ion beam), and complete ref 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA057791V