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Short communication

Enhancement effect of trace H_2O on the charge–discharge cycling performance of a Li metal anode

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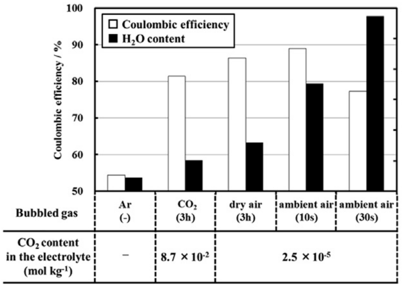
HIGHLIGHTS

- Trace H_2O with CO_2 in the electrolyte enhances the cycling of a Li metal anode.
- The cycling life increases steeply with the increasing the H_2O content up to 35 ppm.
- Enhanced cycling life is observed to be due to the surface products of the SEI.
- Effective SEI layer was produced by way of the reactions related to the trace H_2O.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of a small amount of H_2O with and without CO_2 in an electrolyte of 1 M $LiPF_6$/ethylene carbonate and diethyl carbonate on the cycling life of a Li metal anode is investigated in this paper using charge–discharge cycling. A low cycling performance, which is less than 55%, is observed with the electrolyte with trace H_2O but without CO_2; however, when the trace H_2O is accompanied by CO_2, performance drastically improves and coulombic efficiency reaches a maximum of 88.9%. In the presence of CO_2, the cycling performance is found to be strongly affected by the H_2O content in the electrolyte, and increases with an increase in H_2O content of up to 35 ppm. From an X-ray photoelectron spectroscopy analysis, trace H_2O is found to affect the compounds of the solid electrolyte interphase (SEI) on the lithium surface and produces an Li_2CO_3 and LiF layer on the upper part of the SEI, both known to be good passivation layers for preventing side reactions during charge–discharge cycling.

1. Introduction

Lithium (Li) metal (3860 mAh g^{-1}, 2060 mAh cm^{-3}) shows promise as a negative electrode for use in large-scale energy storage, an increasingly important area owing to the recent emphasis on reducing energy consumption and increasing the use of renewable energy. However, side reactions with the electrolyte solution during charge–discharge cycling and dendritic growth of the Li anode can cause a serious degradation of reversible capacities and the short circuit. The influence of trace H_2O and gas species in ambient air on a lithium metal anode's cycling ability has become an important subject relating to the practical application of the non-aqueous Li–air battery. It has been reported that dissolved CO_2, dry air [1–3], and some additives (vinylene carbonate, fluoroethylene carbonate [4–6], and hydrofluoric acid (HF) [7]) in the electrolyte improve the cycling performance of Li metal anodes and

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restrict the dendritic growth. In particular, Li deposited with CO_2 or dry air has been shown to have a protective effect against large amounts of H_2O and some of the reactive contaminations caused by the products formed on the Li surface during the initial deposition.

This study examines the effect of trace H_2O, with and without CO_2, in 1 M $LiPF_6$/ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte on the charge–discharge cycling lifespan of an Li metal anode, following the procedure proposed by Koch et al. [8]. The enhancement effect of trace H_2O in the presence of CO_2, and the dependence of the cycling performance on the H_2O content in the electrolyte is demonstrated using an electrolyte bubbled with CO_2 gas, dry air, and ambient air.

2. Experimental procedure

Electrochemical characterization was performed in a three-electrode beaker cell. A Ni disk (diameter: 5 mm, purity: 99.99%) was prepared as the working electrode and lithium foils were used for the reference and counter electrode. An electrolyte solution of 1 M $LiPF_6$ (EC : DEC = 50 : 50 volume %), which has a H_2O content of less than 20 ppm was purchased from Kishida Chemical Co., Ltd. The coulombic efficiency of the lithium metal anode was estimated using the charge–discharge cycling test proposed by Koch et al. [8]. Prior to the cycling test, carbon dioxide gas or dry air were bubbled for 3 h in order to saturate the H_2O content in the electrolyte, and ambient air was bubbled for 5, 10, 30, or 60 s.

In this study, 5.1 C cm^{-2} of lithium was initially electrodeposited onto a nickel substrate at 2.0 mA cm^{-2} and then 1.0 C cm^{-2} or 2.4 C cm^{-2} was discharged (dissolved) and charged (deposited) at 2.0 mA cm^{-2} in each subsequent cycle. The end-point of the cycling life was detected by the potential to 1 V vs. Li/Li^+. As for the preparation of the electrolyte, carbon dioxide gas (H_2O content < 50 ppm, purity: 99.99%), dry air (H_2O content < 21 ppm), or ambient air (humidity $= 51 \pm 1\%$) were separately bubbled into their respective pristine electrolytes before the charge–discharge test. The H_2O content in each test solution was measured using the Karl Fischer method (AQ-7, Kyoto Electronics Manufacturing Co., Ltd) and the CO_2 amount was saturated under the partial pressure of the atmosphere. All of the charge–discharge tests were conducted in an Ar-filled glove box with dew point below -110 °C (<1.6 ppb of H_2O).

The elementary chemical state on the Li surface was revealed using X-ray photoelectron spectroscopy (XPS) (VersaProbe-II, ULVAC-PHI). Monochromatic Al–K radiation (1486.6 eV), operated at a power of 25 W (15 kV), was applied as the X-ray source. Sputtering of the sample surface was performed using an Ar^+ ion gun under an accelerating voltage of 3 kV and measurements were made after 0, 2, 4, 6, 8, and 10 min of Ar^+ ion sputtering. All of the samples were washed with pure dimethyl carbonate, dried under a vacuum, and then transferred to chambers using a transfer vessel under an Ar atmosphere.

3. Results and discussion

Fig. 1 shows the coulombic efficiency of the lithium metal anode and the H_2O content in each electrolyte solution, obtained from the electrolytes bubbled with carbon dioxide gas (3 h), dry air (3 h), or ambient air (10 s or 30 s), and the electrolyte that underwent no bubbling. The amounts of lithium at initial deposition and during charge–discharge cycling are 5.1 C cm^{-2} and 1.0 C cm^{-2}, respectively. The amount of dissolved CO_2 in the electrolyte mentioned in this figure was estimated by Henry's law constants [9]. The coulombic efficiency of the unbubbled electrolyte, *i.e.*, with trace H_2O but without CO_2, is less than 55%, but the efficiency obtained with trace H_2O in the presence of CO_2 is over 75%, with a maximum of 88.9%, 34.5% higher than that obtained without CO_2.

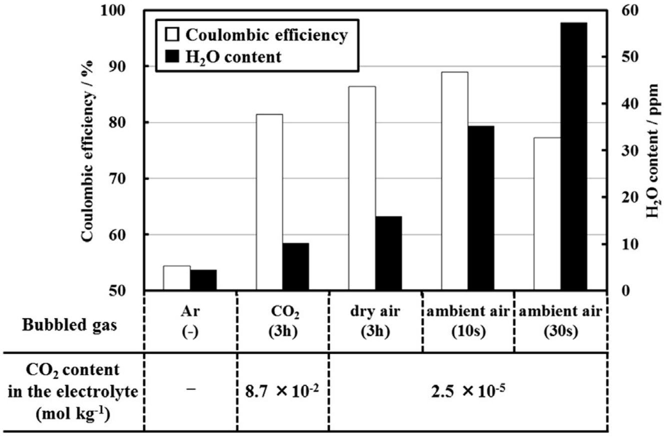

Fig. 1. Effects of H_2O content in the electrolyte bubbled with CO_2 gas (3 h), dry air (3 h), ambient air (10 s and 30 s), and without bubbling on the coulombic efficiency of a lithium metal anode. (The result obtained from the electrolyte without bubbling (*i.e.*, the pristine electrolyte) is described as "Ar (−)" in this figure.).

Enhanced cycling performance caused by the presence of CO_2 gas is still observed, even when an electrolyte solution of EC mixed with DEC was used in place of the propylene carbonate (PC) solution [1]. As for H_2O content, it was slightly increased in the electrolyte that was bubbled with CO_2 gas. The cycling performance obtained with dry air (3 h) is superior to that obtained with CO_2 gas, even though the amount of CO_2 dissolved in the electrolyte with dry air is theoretically the lesser of the two.

In light of the authors' previous report [3], which asserts that dissolved nitrogen (N_2), oxygen (O_2), and argon (Ar) do not improve Li metal cycling performance, this enhanced cycling performance is considered to be due to the effect of both CO_2 and H_2O in the electrolyte. In fact, the H_2O content in the electrolyte bubbled with dry air (3 h) is higher than that with CO_2 gas (3 h). It is also confirmed that the cyclability obtained from the electrolyte bubbled with dry air (6 h) is approximately the same as that with dry air (3 h), since the H_2O content in these electrolytes is nearly equal. The strong dependence of the cycling performance on the amount of H_2O in the electrolyte is observed from the bubbling conducted with ambient air. The coulombic efficiency with ambient air (10 s) is higher than that with CO_2 gas and with dry air (3 h), whereas it is lower with ambient air (30 s).

This result indicates that an optimum H_2O amount exists for achieving the longest cycling life of a lithium metal anode. The reason ambient air (10 s) results in a higher cycling performance than dry air (3 h) is thought to be due to the presence of H_2O in the electrolyte, since the amount of dissolved CO_2 in these solutions is equal. From the results described above, it is concluded that trace H_2O in the presence of CO_2 in the electrolyte plays a significant role in determining the cycling performance of a Li metal anode, and that it also contributes to an increase in cycling performance by a certain amount, regardless of the bubbled gas species, *i.e.*, carbon dioxide gas, dry air, or ambient air.

Fig. 2 shows the coulombic efficiency obtained when the amount of lithium deposited/dissolved during charge–discharge cycling was varied. The amount of lithium during cycling was set to 1.0 C cm^{-2} and 2.4 C cm^{-2} for the right- and left-hand conditions, respectively, with the loading current at 2.0 mA cm^{-2}. The coulombic efficiency is observed to change depending on the coulombic amount of lithium during cycling, and it tends to decrease with an increase in the amount of lithium. Increasing the