Journal of Power Sources 347 (2017) 186–192

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Autoxidation in amide-based electrolyte and its suppression for enhanced oxygen efficiency and cycle performance in non-aqueous lithium oxygen battery

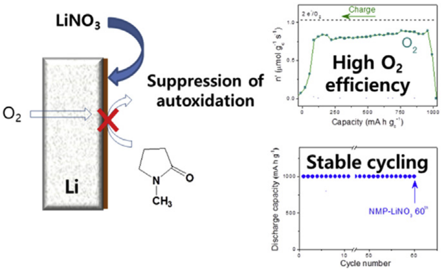
Dong Wook Kim [a], [*], Dong Hun Lee [a], [b], Su Mi Ahn [a], Do Youb Kim [a], Jungdon Suk [a], Dong Hoon Choi [b], Yongku Kang [a], [**]

[a] Advanced Materials Division, Korea Research Institute of Chemical Technology, Yuseong, Daejeon, 305-600, Republic of Korea
[b] Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-Gu, Seoul, 136-701, Republic of Korea

HIGHLIGHTS

- NMP electrolyte is reactive with O_2 gas in the presence of lithium metal.
- Autoxidation is verified by in-situ gas pressure analysis and DEMS.
- Autoxidation results in low O_2 efficiency and fast capacity fading.
- $LiNO_3$ is employed to suppress the autoxidation.
- $LiNO_3$ is efficient in enhancing oxygen efficiency and cycle life.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 November 2016
Received in revised form
14 January 2017
Accepted 10 February 2017

Keywords:
N-methyl-2-pyrrolidone
Autoxidation
Lithium-oxygen battery
Lithium nitrate
In-situ gas pressure analysis

ABSTRACT

In spite of several desirable properties such as high stability against superoxide anion and low vapor pressure, *N*-methyl-2-pyrrolidone (NMP) electrolyte is reported not suitable for use in lithium-oxygen (Li-O_2) batteries because of severe degradation upon cycling and low oxygen efficiency. In this work, we find that NMP electrolyte is reactive with O_2 gas in the presence of lithium metal and such O_2-consuming reaction (*i.e.*, autoxidation) is a possible cause for the poor performance in Li-O_2 batteries with NMP electrolyte. The autoxidation of NMP is verified by direct measurement of the depletion of O_2 gas in the hermetically sealed symmetric Li/Li cells via in-situ gas pressure analysis. In-situ differential electrochemical mass spectroscopy (DEMS) experiment reveals that the autoxidation resulted in significant O_2 consumption upon discharge, very low O_2 efficiency upon charge, and eventually fast capacity fading. Lithium nitrate ($LiNO_3$), which provides a protective layer on the surface of lithium metal, is employed to suppress the autoxidation, leading to significantly enhanced oxygen efficiency and cycle life.

1. Introduction

Lithium-oxygen (Li-O_2) batteries have attracted a great deal of research interests from the academia and industrial sectors owing to their high theoretical energy density comparable with gasoline for possible application in range-anxiety-free electric vehicles [1–12]. The initial promise of Li-O_2 batteries, however, has subsided upon the realization of serious technical issues with the batteries, such as low oxygen efficiency, high over-potential upon charge, and fast capacity fading upon cycling [13–19]. Because these critical problems mainly originate from degradation of the

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: dongwook@krict.re.kr (D.W. Kim), ykang@krict.re.kr (Y. Kang).

http://dx.doi.org/10.1016/j.jpowsour.2017.02.027

electrolytes, development of stable electrolytes is considered an urgent task for realizing rechargeable Li-O_2 batteries [20–24]. Among the candidates for Li-O_2 battery electrolytes, amide-based electrolytes such as dimethylacetamide (DMA) are considered promising owing to their superior stability against the nucleophilic attack of superoxide anions [25]. Several researchers recently reported that DMA electrolytes exhibited stable rechargeability over 80 cycles, with low over-potential and high O_2 regeneration upon charge [26–28]. However, the relatively low boiling point of DMA results in a high vapor pressure, making it unsuitable for practical Li-O_2 battery applications because of the open structure of the cell.

N-methyl-2-pyrrolidone (NMP) is a family of amide solvents with a cyclic structure. Its higher boiling point (202 °C for NMP as compared to 165 °C for DMA) and hence ten times lower vapor pressure as compared to DMA (0.29 mmHg for NMP as compared to 2.70 mmHg for DMA at 20 °C) is highly attractive. The Gibbs free energy of activation (ΔG_{act}) for nucleophilic attack by superoxide anion onto NMP calculated by density-functional theory (DFT) is known to be relatively high and comparable to that of DMA [29]. In spite of the above mentioned superior characteristics, however, NMP electrolytes have been reported not suitable for use in Li-O_2 cells because of severe degradation upon cycling and low oxygen efficiency [30–32]. A detailed study using Fourier transform-infrared (FT-IR), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD) analysis on Li-O_2 cells of NMP electrolyte with lithium perchlorate ($LiClO_4$) by Chen et al. [30] showed that after the discharge process, only side-products such as lithium carbonates and carboxylates were detected instead of the desired lithium peroxide (Li_2O_2). The mass spectrometric cyclic voltammograms by Bondue et al. [31] revealed that the oxygen efficiency of NMP electrolytes was only ~25% upon cycling. Wang et al. [32] observed only 20% residual capacity in just five cycles and attributed the fast capacity fading to degradation of the NMP electrolytes, which was confirmed by X-ray photoemission spectroscopy (XPS).

In this work, we find that NMP electrolyte is reactive with O_2 gas in the presence of lithium metal and that such O_2-consuming reaction (*i.e.* autoxidation) is a possible main cause for the poor performance in the Li-O_2 batteries with NMP electrolyte. The autoxidation reaction was verified by several experimental methods including in-situ gas pressure analysis, FT-IR, and in-situ differential electrochemical mass spectroscopy (DEMS). For viable Li-O_2 battery operation, the autoxidation of NMP should be suppressed. Lithium nitrate ($LiNO_3$), which is known to provide a protective layer on lithium metal [26,33], was applied to prohibit the NMP electrolyte from coming into contact with the lithium metal, resulting in greatly enhanced oxygen efficiency and cycle performance.

2. Experimental

2.1. Preparation of electrolytes

N-methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich Chem. Co.) was purified by vacuum distillation and dried with activated 4 Å molecular sieves before use. Lithium nitrate ($LiNO_3$, 99.99%), lithium trifluoromethane sulfonate ($LiSO_3CF_3$, 99.995%), and lithium perchlorate ($LiClO_4$, 99.99%) were obtained from Sigma-Aldrich Chem. Co. and dried in a vacuum oven at 150 °C for 2 days. NMP electrolytes were prepared by dissolving the lithium salts in NMP solvent as a concentration of 1 M. The water content of the electrolytes was controlled to less than 20 ppm, which was measured by Karl Fischer titration (C30, Mettler Toledo).

2.2. Preparation of Li-O_2 cells

Swagelok-type Li-O_2 cells were assembled according to the method described in the previous papers [9,24]. The Li-O_2 cells were composed of Li metal as an anode, a glass microfiber membrane as a separator, and a Ketjenblack® (KB, EC-600JD, AkzoNobel Co.) carbon electrode as a cathode. The carbon electrode was prepared by coating a slurry, which was a mixture of KB (90 wt%) and polytetrafluoroethylene (PTFE) binder (10 wt%) in isopropyl alcohol, onto Teflon-treated carbon paper (TGP-H030, Toray Co.). The coated carbon cathode was thoroughly dried at 150 °C in a vacuum oven and then transferred to an argon-filled glove box for cell assembly. The KB carbon was typically loaded at 0.5 mg cm^{-2}.

2.3. In-situ gas pressure analysis

Autoxidation of the NMP electrolytes was assessed by in-situ gas pressure analysis, which directly measured the amount of oxygen gas consumed in the hermetically sealed Swagelok-type cells. NMP electrolyte-soaked separators (typical amount of NMP electrolyte was 0.1 mL) were sandwiched between two lithium metal foils, resulting in symmetric Li/Li cells, which were then used for in-situ gas pressure analysis. The Li/Li cells, which had tightly capped capillaries, were transferred from the glove box to the in-situ gas pressure analysis system. Analysis was performed by using a differential electrochemical mass spectrometry (DEMS) set-up, in which a pressure sensor (UNIK 5000, GE, pressure range: −1~7 bar, accuracy: ±0.1% full scale) was placed in line to measure the gas pressure change in the cell headspace [9]. At first, the symmetric Li/Li cells were fed by argon gas (>99.999%), and then approximately 40 min later, the argon was replaced by O_2 gas (>99.999%). The pressure drop in the symmetric Li/Li cells was monitored in real time during the test. Given the volume of the cell headspace, the measured pressure change in the cells could be translated to the molar amount of gas using the ideal gas law.

2.4. Fourier transform-infrared measurements

After in-situ gas pressure analysis, the symmetric Li/Li cells were disassembled. The electrolyte-soaked separators were investigated by Fourier transform-infrared (FT-IR) spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc.) with an attenuated total reflectance (ATR) accessory, in which a monolithic diamond crystal was mounted. Disassembly of the cells and FT-IR measurement on the separators were carried out in a dry room, in which moisture is controlled less than 100 ppm.

2.5. ^{1}H nuclear magnetic resonance measurements

The separators, which were taken from the disassembled Li/Li cells after in-situ gas pressure analysis, were dried in the antechamber of the glove box. The separators were then washed with deuterated NMR solvent ($CDCl_3$) to extract the autoxidized NMP product. ^{1}H NMR spectra were recorded with a Bruker model DRX-300 spectrometer (Bruker Instruments, Germany).

2.6. In-situ DEMS analysis

In-situ DEMS analysis was conducted for quantitative evaluation of O_2 consumption during discharge, and evolution of O_2 and other gaseous side products during charge process in the Li-O_2 cells. Details of the set-up and method used are described in our previous papers [9,24]. Several parameters obtained from the DEMS experiment are defined as follows. The oxygen efficiency at discharge, $(\eta_{O2})_{dis}$ is the ratio of O_2 quantity consumed on discharge compared