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Discharge Li-O_2 batteries with intermittent current

Fangzhou Wang, Xianglin Li*

Department of Mechanical Engineering, University of Kansas, Lawrence, KS 66046, USA

HIGHLIGHTS

- Applying intermittent current (>1 mA/cm^2) enhances O_2 diffusion in the electrode.
- The battery capacity is increased by more than 50% with intermittent discharge.
- Hydrophilic electrodes benefit the most from the intermittent discharge strategy.
- Discharging with descending currents maximizes capacity with a given cutoff voltage.

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ABSTRACT

This study periodically rests Li-O_2 batteries (for 5–10 min) between each 2–10 min discharge to improve the oxygen transfer within the porous electrode. Periodically resting the battery increases the specific discharge capacity by at least 50% at various current densities (0.1–1.5 mA/cm^2). Multistep discharge at decreasing current rates (2.0, 1.5, and 1.0 mA/cm^2) is also proposed to increase the overall discharge capacity with a given cutoff voltage. The performance improvement is mainly due to the enhanced O_2 diffusion during rest between intermittent discharge. The lyophilic electrode has the highest increase rate of discharge capacity after applying intermittent current while the electrode with mixed wettability achieves the highest specific discharge capacity. The resting and discharging time of electrodes with mixed wettability are then optimized at 1.0 mA/cm^2. Cycling tests with 1000 mA h/g and 1500 mAh/g cut-off capacities at 1.0 mA/cm^2 are also performed. The batteries completed similar numbers of cycles with a higher cut-off capacity (1500 mAh/g) applying intermittent discharge, compared with applying continuous current (1000 mAh/g cut-off capacity). This study emphasizes the importance of O_2 diffusion and provides practical strategies to improve the deep discharge capacity of Li-O_2 batteries, especially at high current rates (>1.0 mA/cm^2).

1. Introduction

The rapid growth in technologies such as electrical vehicles and mobile electronic devices and the urgent need to reduce environmental pollution require energy storage systems with higher energy density. Nowadays, Li-ion batteries have been commercialized and widely utilized for decades but the energy density of the state-of-art Li-ion batteries (~300 Wh/kg) is limited by the intercalation chemistry. The Li-O_2 battery is considered at one of the most promising energy storage technology replacing Li-ion battery due to the extremely high theoretical energy density of ~3500 Wh/kg [1,2]. The electrochemical reactions occurring in Li-O_2 batteries are shown in Eqs. (1)–(3). The theoretical voltage of the reaction E^0 is 2.96 V [3].

$$\text{Anode: } 2\text{Li} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2\text{Li}^+ + 2e^- \tag{1}$$

$$\text{Cathode: } 2\text{Li}^+ + 2e^- + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \text{Li}_2O_2 \tag{2}$$

$$\text{Overall: } 2\text{Li} + O_2\text{Li} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \text{Li}_2O_2 \tag{3}$$

When the Li-O_2 batteries are discharged, the Li metal is oxidized to Li^+ at the anode and O_2 is reduced on the cathode, generating solid Li_2O_2. During charge, the reversed cathodic reaction decomposes Li_2O_2 and releases O_2 and Li^+. The Li metal is deposited on anode by the reversed anodic reaction. Although the above electrochemical reactions have extremely high theoretical energy density, the practical energy density is only ~1000 Wh/kg [4]. Multiple challenges exist in developing Li-O_2 batteries for commercial applications. The fundamental issues related to Li-O_2 batteries, including the reaction mechanism, the electrochemical stability of cathode, electrolyte and Li anode are not be fully understood [5,6]. Besides, the low discharge/charge rate

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* Corresponding author.
E-mail address: xianglinli@ku.edu (X. Li).

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capability, poor cycle life and low round-trip efficiency are the crucial factors that impede the practical operation of Li-O_2 batteries [7–9]. Research find that the reaction over-potential is mainly caused by cathode reactions [10]. The cathode passivation deteriorates as the discharge current density increases and the discharge current density is a key parameter that can affect the performance of Li-O_2 batteries.

The practical applications of electrical vehicles require discharging the current density that is two orders of magnitude higher than the present current density applied in discharging the Li-O_2 batteries (e.g. 0.1 mA/cm^2) [11]. Therefore, it is urgent to discharge the Li-O_2 batteries at higher current density to facilitate the commercialization. Multiple numerical and experimental studies demonstrated that the discharge capacity would be reduced significantly if the Li-O_2 batteries are discharged at high current density [12–19]. For instance, Han et al. [14] stated that the discharge voltage plateau decreased by 0.2 V and discharge capacity decreased from 6219 to 1251 mAh/g when the current density increases from 0.1 mA/cm^2 to 0.4 mA/cm^2. Mohazabrad et al. [19] showed that the specific discharge capacity decreased from 461.53 mAh/g to 106.07 mAh/g when the current density increased from 0.1 mA/cm^2 to 0.5 mA/cm^2. Tremendous efforts have been paid to clarify the dominated factor that affect the discharge capacity of Li-O_2 batteries at high current density. The electrical passivation of cathode caused by Li_2O_2 film and poor O_2 transportation limited by pore clogging are claimed as two major factors that limit the discharge capacity. For example, Adams et al. [20] reported that Li_2O_2 particles nucleated at low current densities (5–25 μA/cm^2), and amorphous thin films of Li_2O_2 formed by electro-reduction reaction on the electrode surface at high current densities (50–100 μA/cm^2). The investigation by Adams et al. [20] also showed that the direct electron transfer would incur a significant voltage drop at high current density which indicates the thickness and conductivity of the Li_2O_2 film become more important for discharging Li-O_2 batteries at high current density. The electrical conductivity of Li_2O_2 film was investigated both experimentally and numerically [21]. Results show that the critical thickness of Li_2O_2 film is ~5 nm above which the exchange current density fell rapidly below ~10^{-7} A/cm^2 and the ORR was no longer supported, leading to “sudden death” of Li-O_2 batteries. The electrical conductivity of Li_2O_2 was estimated to be in the range of 10^{-12} to 10^{-13} S cm^{-1} and the critical thickness of 5 nm was confirmed by Lu et al. [22]. Mirzaeian et al. [16] examined the operation effect on the performance of Li-O_2 batteries systematically. The discharge capacity decreased from 2387 mAh/g to 364 mAh/g as the current density varied from 10 mA/g to 150 mA/g. The discharge ceased when the discharge products occupied almost all the pores at lower current density. Another study [23] argued that the Li_2O_2 deposition only covers the electrode external surface by forming a thin film rather than filling the interior pores in the electrode at high current density. Therefore, the capacity loss can be attributed to the fast deposition of Li_2O_2 on the electrode surface which limits the transportation of O_2 and Li^+ and blocks the inner active surface. However, the morphology of discharge products such as the primary product of Li_2O_2 is not only influenced by the current density but other factors such as the electrode structure [24] and the electrolyte [25,26]. Thus, it is very challenging to control the morphology of discharge products to improve the rate capability of Li-O_2 batteries.

On the other hand, studies [27,28] claimed that the poor rate capability of Li-O_2 batteries was mainly due to sluggish O_2 transportation in the organic electrolyte of flooded electrodes, which was also reported by the numerical studies [13,29]. The 1 M electrolytes with different constituents display various viscosity such that the corresponding O_2 diffusion coefficients estimated by Stokes-Einstein equation are also different [28]. For example, 1 M Li hexafluorophosphate ($LiPF_6$) in propylene carbonate (PC) has the viscosity of 8.06 cP while the viscosity of 1 M LiPF6 in PC: dimethoxyethane (DME) (1:2) is 1.98 cP. When discharge the Li-O_2 batteries with 1 M $LiPF_6$/PC and 1 M $LiPF_6$/PC:DME (1:2) at 0.1 mA/cm^2, the discharge capacities were 380 and 1095 mAh/g, respectively. When discharging those batteries at 0.5 mA/cm^2, the discharge capacity corresponding to 1 M $LiPF_6$/PC was 85 mAh/g while it was 363 mAh/g for 1 M $LiPF_6$/PC:DME (1:2). The three times increase of capacity showed that promoting O_2 diffusion in the electrode can reduce the capacity loss at high current density. In other words, the poor O_2 diffusion may dominate the performance of Li-O_2 batteries at high current density.

The debate on the determining factor of capacity loss of Li-O_2 batteries at high current density may continue until the fundamental mechanism is fully understood. However, possible approaches which include intermittent operating procedure and modifying the electrode wettability [30] can be applied to enhance the O_2 diffusion in the electrode and thus improve the rate capability of Li-O_2 batteries. In this study, intermittent discharge strategies were proposed and investigated for Li-O_2 batteries with electrodes of different wettability at various current densities (0.1–2.0 mA/cm^2), and compared with batteries discharged at continuous current densities. Cycling experiments on Li-O_2 batteries were also studied to determine the effect of discharge strategy on discharge-charge cycles.

2. Experimental methodology

The cathode electrode used in this study was prepared by coating conductive acetylene black (MTI Corporation) on the AvCarb 1071 HCB plain carbon cloth (Fuel Cell Store) [30]. Firstly, the acetylene black was mixed with the binder such as polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF) at 15% mass fraction in ethanol solution. After dipping the substrate carbon cloth in the slurry and drying it in the atmosphere for 24 h for three times, the electrode was heat treated at 350 °C for 30 min. The electrodes containing 15% PVDF carbon coatings and the ones with mixed layers of carbon coatings (both 15% PTFE and 15% PVDF) were also prepared as described above. The structures of three types of the customized electrodes are shown in Figure S1. The measured carbon loadings of the fabricated electrodes were 3.0 ± 0.2 mg/cm^2.

The battery structure was displayed in Fig. 1 and the oxygen diffuser, customized cathode electrode, separator and Li chip are compressed together to guarantee the good contact between each component. The open ratio of oxygen diffuser was 50% [18] and the separator was a Whatman GF/B glass fiber filter from Fisher Scientific with the diameter of 2.1 cm. The PTFE gasket and O-ring were inserted between current collectors to avoid the short circuit and prevent O_2 leaking. The electrolyte consisted of dissolving bis(trifluoromethylsulfonyl)amine Li salt (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME). The concentration of prepared electrolyte was 1 M and the volume added in the battery was 120 μL. All these fabricating processes were completed in the Mikrouna glovebox with water and oxygen concentrations less than 1 ppm.

The electrochemical performance of the Li-O_2 batteries were examined by a 4-channel Arbin MSTAT4 battery tester at room temperature (20 °C). All the tests were set with the discharge cut-off voltage of 2.0 V, unless stated otherwise. Each group of the test was initiated after resting the battery for 1 h and repeated at least three times. All the experimental cases, with different combinations of discharge strategies and various customized electrodes, were listed in Table S1. The discharge strategies included continuous current and intermittent current at which the Li-O_2 batteries were discharged and rested periodically.

The acetylene black carbon is examined using a N_2 adsorption technique. The physisorption measurement is performed at 77 K by the surface and pore size analyzer (NOVAtouch N2TLX – 1, Quantachrome Instrument, U.S.). The sample weight is approximate 0.1 g which is degassed at 300 °C for 3 h before adsorption/desorption measurements. The amount adsorbed vs. the adsorptive pressure (P), relative to the saturated vapor pressure over the bulk liquid (P_0) is obtained and used for analysis. According to the isotherms of adsorption and desorption, the surface area is analyzed by Brunauer, Emmet and Teller (BET) method, the pore size distribution is evaluated by Barrett, Joyner and