Experimental Studies of Carbon Electrodes with Various Surface Area for Li−O_2 Batteries

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Abstract for Social Media

Electrodes made from recycled tea leaves is demonstrated for the first time in Li−O2 batteries. The waste tea leaves are recycled from household tea leaves and activated using KOH. This study confirms that mixtures of carbon material with different specific surface areas can increase the discharge capacity. The battery reached the discharge capacity of 3.88 Ah/g at 0.5 mA/cm2 when the electrode is made from 70wt% recycled tea leaves and 30wt% of Vulcan XC 72 carbon. Recycled tea leaves can reduce the manufacturing cost of battery and make it a more economically feasible technology.

Abstract

Li−O_2 batteries with carbon electrodes made from three commercial carbons and carbon made from waste tea leaves are investigated in this study. The waste tea leaves are recycled from household tea leaves and activated using KOH. The carbon materials have various specific surface area and porous structures were characterized by the N_2 adsorption/desorption. Vulcan XC 72 carbon shows a higher specific surface area (264.1 m^2/g) than the acetylene black (76.5 m^2/g) and Super P (60.9 m^2/g). The activated tea leaves have an extremely high specific surface area of 2868.4 m^2/g. Firstly, we find that the commercial carbons achieve similar discharge capacities of ~2.50 Ah/g at 0.5 mA/cm^2. The micropores in carbon materials result in the high specific surface area but cannot help to achieve higher discharge capacity because it cannot accommodate the solid discharge product (Li_2O_2). Mixing the acetylene black and the Vulcan XC 72 improves the discharge capacity due to the optimized porous structure. The discharge capacity increases by 42% (from 2.73 ± 0.46 to 3.88 ± 0.22 Ah/g) at 0.5 mA/cm^2 when the mass fraction of Vulcan XC 72 changes from 0 to 0.3. Secondly, the electrode made from activated tea leaves is demonstrated for the first time in Li−O_2 batteries. Mixtures of activated tea leaves and acetylene black confirm that mixtures of carbon material with different specific surface areas can increase the discharge capacity. Moreover, carbon made from recycled tea leaves can reduce the cost of the electrode, making electrodes more economically achievable. This study practically enhances the discharge

capacity of Li−O_2 batteries using mixed carbons and provides a method for fabricating carbon electrodes with lower cost and better environmental friendliness.

Keywords: Li-O_2 Battery; Carbon Electrode; Specific Surface Area; Discharge Capacity; Tea Leaves

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1. Introduction

Severe environmental issues such as increasing levels of greenhouse gas emission have occurred in the recent a few decades due to the rapid increase of fossil fuel consumptions. As a result, the electric vehicle usually powered by lithium-ion batteries is considered a promising candidate to replace the traditional vehicle and reduce the environmental pollution.[1-2] However, the lithium-ion battery cannot fully meet the requirement of high energy density, limited by the theoretical energy density of the lithium-ion battery (~600 Wh/kg).[3] This is mainly due to the nature of the crystalline structure and the electrochemical properties of its cathode materials such as $LiCoO_2$ and $LiFePO_4$.[4-6] Recently, the Li−O_2 battery has become more popular due to the extremely high energy density of lithium metal (~11,680 Wh/kg).[7] This value is close to the theoretical energy density of gasoline of 13,000 Wh/kg. Nonetheless, the practical energy density is about 10 times lower the theoretical value. The achievable energy density of Li−O_2 battery is estimated between 500 and 900 Wh/kg in the state-of-the-art literature.[8] Therefore, paramount attentions have been devoted to understanding the drawbacks that hinder the achievement of the high energy density of Li−O_2 batteries.

In general, Li−O_2 batteries have been classified into four categories based on the type of the electrolyte: aprotic, aqueous, all-solid-state, and hybrid aqueous/aprotic.[9] The major research has focused on the aprotic Li−O_2 battery due to the sufficient ionic conductivity of the aprotic electrolyte and prevention of Li anode corrosion.[10-11] Thus, the Li−O_2 battery in this study refers to the aprotic type. The typical structure of a Li−O_2 battery is comprised of the Li metal anode, the porous cathode electrode and the aprotic electrolyte with a dissolved lithium salt.[9] In addition, basic electrochemical reactions happening during the operation of the Li−O_2 battery are described in Eq. 1−Eq.3 and the open circuit voltage is 2.96V[12].

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

$$\text{Cathode: } 2Li^+ + 2e^- + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2 \quad (2)$$

$$\text{Overall: } 2Li + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2 \quad (3)$$

Studies targeting to improve the practical energy density of Li−O_2 batteries typically tackle with the three components and the reaction mechanisms. For example, aprotic electrolytes can be decomposed by the attack of active discharge species such as O^{2-}, LiO_2, and LiO^{2-} [13]. The Li anode dendrite formation limits the discharge capacity and imposes a severe safety threat on the operation of Li−O_2 batteries.[14-15] The cathode should be able to conduct the ions and electrons effectively and be stable against the discharge/charge species. Additionally, the fast O_2 diffusion is also essential to ensure the high performance of Li−O_2 batteries. Various studies have been conducted on the cathode, mainly including research on cathode materials,[16-18] cathode structure[19-27], and cathode wettability.[28-30] For instance, Wang et al.[28] investigated effects of electrode wettability on the discharge capacity of the Li−O_2 battery. It was concluded that the lyophobic electrode achieved more than 2.0 Ah/g discharge capacity than that of the lyophilic electrode by promoting the O_2 diffusion. The electrode with mixed wettability can balance the number of reaction sites and the number of the fast diffusion paths in the electrode, which resulted in the highest discharge capacity of 5.15 Ah/g. Furthermore, the distribution of active sites for electrochemical reactions and the dry regions for fast O_2 diffusion are determined by the microstructure[31-32] (i.e., specific surface area and porosity) and the electrode composition (i.e., binder, catalyst, and carbon particle).[33-34]

Unlike the electrode in the cathode in other electrochemical devices such as fuel cells, the cathodic electrode in the Li−O_2 battery has a bifunctional role. On one hand, the gas and charged species are transferred in the porous electrode, one the other hand, the electrode serves as a reservoir to accommodate insoluble discharge products (i.e., Li_2O_2).[35] Previously, it assumed that pore-clogging can be the main factor resulting in the "cell death" in the Li−O_2 battery.[36] The porous electrode cannot provide enough space to accommodate the discharge product so that the discharge capacity of the Li−O_2 battery is limited. However, several studies[37-38] showed that the passive layer of discharge products was regarded as the main factor to determine the discharge capacity of the Li−O_2 battery. In our previous study,[29] the discharged electrodes were measured by the scanning electron microscope (SEM). Results showed that the morphology of the main discharge product (Li_2O_2) was affected by the discharge current. The needle-like particles were detected at low current while the film-like discharge products were deposited on the electrode surface at high current. The dependence of the morphology on the discharge current has been confirmed by other studies.[39] The discharge capacity is dominated by the O_2 diffusion in the porous electrode, especially at high discharge current.[29] Besides, the cathode electrode derived from metal organic

frameworks (MOFs) can also increase the discharge capacity and stabilize the discharge voltage plateau of the Li−O_2 battery, which is due to hierarchical mesoporous nanocomposites.[40-41] Hence, it is worthwhile to pay more attention to the structure of the porous electrode.

All the research mentioned above imply that the discharge capacity of the Li−O_2 battery is proportional to the active carbon surface in the porous electrode. The active carbon surface which refers to the reaction sites should be able to access the electrolyte and the O_2. In general, the discharge capacity should increase when the active specific surface area increases. However, only a few studies focus on the influence of the specific surface area in the porous electrode.[22, 36, 42] Meini et al.[22] investigated the effect of carbon (e.g., Vulcan XC 72, BP2000 and KB600) specific surface area on both the first discharge capacity and the cycling performance of the Li−O_2 battery. The surface normalized discharge capacities of all the electrodes were similar and the passivating Li_2O_2 layer was deposited on the carbon surface. Besides, other studies found that the discharge capacity increased with the total volume of mesopores[42] and was proportional to the average pore diameter.[34] However, the above studies did not investigate the carbon electrode with mixed type of carbons. Zhang et al.[43] paid attention to the use of mixed carbon materials. It was found that the carbon mixture of KB600 and Super P could increase the discharge capacity by enhancing the O_2 mass transport.

The porous electrode of a Li−O_2 battery should use the environmentally friendly and cost-effective materials.[44] In this study, electrodes were fabricated from different carbons, including both commercial carbon blacks (i.e., acetylene black, Super P, and Vulcan XC 72) and carbon materials activated from recycled tea leaves. Moreover, mixed carbons were also coated on the carbon cloth substrate to fabricate electrodes. Porous structures of all electrodes were characterized by the N_2 adsorption/desorption technique. Li−O_2 batteries with electrodes coated by commercial carbons and their mixtures were discharged at 0.5 mA/cm^2. Discharge performances of carbon made from activated tea leaves and the mixture of acetylene black and activated tea leaves were tested. In addition, an electrode of activated tea leaves was discharged at 0.5 mA/cm^2 to examine the effect of specific surface area on the discharge capacity.

2. Experimental Methodology

Electrode fabrication: All commercial materials purchased in this study were used as received. Three commercial carbon blacks (acetylene black, Super P and Vulcan XC 720) were purchased

from MTI Corporation and used as such to prepare the porous electrode for the Li−O_2 battery. Meanwhile, wasted tea leaves were recycled and activated to generate carbon materials for porous battery electrodes.[45] The dried household tea leaves were carbonized directly at 350 °C for 2 hours. Afterward, KOH and carbonized tea leaves were grounded and mixed (1:3 wt. ratio) uniformly, after which the mixture was pyrolyzed at 800 °C for 2 hours under the N_2 atmosphere. Finally, the resulted powders were washed by 1 M HCl solution and dried overnight before usage. Different carbon materials were also mixed together to prepare porous electrodes. All mixtures are listed in Table 1. Each type of carbon was mixed with polytetrafluoroethylene (PTFE) binder (85:15 wt%. ratio) in ethanol solution. The corresponding slurry was sonicated for 1h to ensure that the carbons and binders were well mixed. The AvCarb 1071 HCB plain carbon cloth was dipped in the slurry and dried in the atmosphere for three times. The electrode was finished after the heat treatment at 350 °C for 30 minutes. The measured carbon loading of each electrode (1.26 cm^2) is 2.8~3.3 mg.

Table 1. Mixtures of different carbons for the electrode preparation.

Name	Carbons	Weight ratio
Mixture_1	Acetylene black + Vulcan XC 72	9:1
Mixture_2	Acetylene black + Vulcan XC 72	8:2
Mixture_3	Acetylene black + Vulcan XC 72	7:3
Mixture_4	Acetylene black + Activated tea leaves	5:5
Mixture_5	Acetylene black + Activated tea leaves	9:1

Electrolyte: Long chain ethers were reported to be stable and have less volatility and polarity.[9] Tetraethylene glycol dimethyl ether (TEGDME) was selected as the electrolyte solvent due to its stability against superoxide species.[46] The bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) was dissolved in the TEGDME and the concentration of electrolyte was 1 M.

Battery assembly and testing: The prototype of a Li−O_2 battery[47-48] was designed and assembled based on the schematic in Figure 1. The customized electrode was inserted in the battery as the cathode and the lithium chip with the diameter of 1.56 cm (MTI Corporation) was placed as the anode. The separator was the Whatman GF/B glass fiber filter with the diameter of 2.1 cm. Moreover, the oxygen diffuser with 50% open ratio was inserted to distribute the O_2 more uniformly and reduce the electrolyte evaporation. 120 μL electrolyte was added before assembling all components. Li−O_2 batteries were fabricated in the glovebox (Mikrouna) with water and

oxygen concentrations less than 1 ppm. Experiments of discharging Li−O_2 batteries were performed by a 4-channel Arbin MSTAT4 battery tester at room temperature (20 °C). The cut-off voltage for discharge was 2.0 V.

N_2 adsorption/desorption: All carbon samples, including commercial carbons, activated tea leaves and carbon mixtures, were characterized by the surface and pore size analyzer (NOVAtouch N2TLX – 1, Quantachrome Instrument, U.S.). Isotherms of adsorption and desorption were obtained by the physisorption measurement performed at 77 K. After acquiring the isotherms, the Brunauer, Emmet, and Teller (BET) method was employed to analyze the specific surface area and the Barrett, Joyner, and Halenda (BJH) method was utilized to evaluate the pore volume and pore size distribution.

3. Results and Discussion

A summary of the structural properties of different carbon materials is shown in both Table 2 and Figure 2. Moreover, the obtained isotherms are shown in Figure 3. The type IV isotherms are observed clearly for the acetylene black and Super P in N_2 adsorption/desorption measurement, which indicates mesoporous structures in corresponding electrodes. The total specific surface area of ~70 m^2/g mainly results from mesopores. Isotherms of other carbon samples have the characteristics of both type I and type IV, indicating that both the micropores and mesopores exist in samples. For example, activated tea leaves have an extremely high specific surface area of 2868.4 m^2/g which is confirmed by the previous study.[45] The high specific surface area is due to the large proportion of micropores. The microporous specific surface area of the tea carbon is 2091.1 m^2/g. In addition, the SEM image of difference carbon simples are shown in Figure 4. Higher porosity is observed in carbon made from activated tea leaves, which is obviously different from commercial carbons. When the acetylene black and Vulcan XC 72 are mixed together, the total specific surface area increases with the mass fraction of Vulcan XC 72, which is mainly attributed to the increase of micropores. The same trend has also been found in the mixture of activated tea leaves and acetylene black. Generally, commercial carbons known as highly-structured because primary particles (15−50 nm) are fused together during the fabricating procedure.[49] Figure 2 (b) shows that the pores in the acetylene black and Super P belong to the mesopores, especially in the range of 2–10 nm in diameter. However, both the micropores and mesopores exist in all the other carbon samples. Micropores are not detected in mixture_1 which

may be due to the insufficient amount of the sample. Typically, the mixture of different carbons can increase the total specific surface area of the porous electrode by providing more micropores. The total specific pore volume and specific micro volume of each carbon are also shown in Table 2. Generally, the specific pore volume shows similar trend as that shown in the specific surface area. The specific micro pore volume of acetylene black and Super P carbon is zero due to lack of micro pores. Conversely, micro pores exist in Vulcan XC 72 and activated tea leaves. When the mass fraction of micro pores increases, more specific pore volume will be attributed to specific micro pore volumes. Discharge performances of different customized electrodes will be shown and discussed in the following section.

Table 2. The specific surface area and pore volume of different carbon samples.

Sample	S_{total} (m^2/g_c)	S_{micro}[a] (m^2/g_c)	$S_{external}$[b] (m^2/g_c)	V_{total} (cc/g)	V_{micro}[c] (cc/g)
Acetylene black	76.5	0	76.5	0.25	0
Super P	60.9	0	60.9	0.16	0
Vulcan XC 72	264.1	97.5	166.6	0.43	0.05
Activated Tea leaves	2868.4	2091.1	777.3	1.16	1.03
Mixture_1	87.8	0	87.8	0.24	0
Mixture_2	108.3	4.2	104.1	0.26	0.002
Mixture_3	135.9	7.5	128.4	0.25	0.001
Mixture_4	259.1	194.3	64.8	0.12	0.08
Mixture_5	135.7	91.3	44.4	0.16	0.1

[a] S_{micro} stands for the specific surface area of micropores (diameter < 2 nm). [b] $S_{external}$ represents the surface of pores with a diameter larger than 2 nm. [c] V_{micro} stands for the specific pore volume of micropores (diameter < 2 nm).

Currently, it is urgent to promote the commercialization of the Li−O_2 battery to meet the demand of the electric vehicles. Discharging the battery at higher current density can facilitate the commercialization.[30, 50] In this study, Li−O_2 batteries with electrodes made from commercial carbons are firstly discharged at a very high current density of 0.5 mA/cm^2. Despite the fact that the Vulcan XC 72 has the largest specific surface area, three commercial carbons achieve similar discharge capacities of 2.50 Ah/g shown in Figure 5. The previous studies suggest that the carbon electrode with higher mesoporous volume can enhance the discharge capacity.[44, 51] The volume of

micropores does not have significant impacts on the discharge capacity because the micropores cannot accommodate the discharge products such as the Li_2O_2. Even the mesoporous specific surface area in the Vulcan XC 72 is 166.6 m^2/g, the mesopore volume has not been fully utilized. The electrode surface of mesopores can be active only when it is accessible to O_2 and electrolyte. It is speculated that the micropores may block the effective use of the mesopores. Therefore, electrodes with mixed carbon materials are tested and shown in Figure 6. When mixing the acetylene black with the Vulcan XC 72, the discharge capacity increases from 2.73 ± 0.46 to 3.88 ± 0.22 Ah/g as the mass fraction of the Vulcan XC 72 increases from 0 to 0.3. Mixed carbons can improve the accessibility of oxygen and electrolyte to active sites and thus increase the discharge capacity. This observation agrees well with previsouly published results.[43] The discharge capacity does not exhibit a proportional relationship with the total pore volume. Though Vulcan XC 72 R has more mesopore volume than acetylene black and Super P, its discharge capacity is less which demonstrates that mesopore pore volume is not effectively utilized. Mixing acetylene black and Vulcan XC 72 R can improve the usage of meso pore volume which promotes the discharge capacity. In addition, the electrode with only acetylene black is lyophobic[28] but the lyophobicity will decrease as the Vulcan XC 72-R carbon is added. The lyophobic electrode can reserve more dry surfaces so that the O_2 diffusion can be facilitated. Generally, lyophobic electrodes can obtain higher discharge capacity than lyophilic ones.[28] Therefore, the wettability should also be taken into account when considering the enhanced discharge capacity. In this study, the mass fraction of PTFE binder is 15% in all electrodes, ensuring the variations of discharge capacity can be mainly attributed to the differences of specific surface area. The coupled effects of the specific surface area and the wettability[34] will be focused on in the future.

Although numerous efforts have been devoted to optimizing the structure of cathode electrodes, reducing the cost and using more natural materials are also important for the development of $Li-O_2$ batteries. Carbon materials such as carbon nanotubes and graphene can achieve decent discharge capacity but the high cost imposes negative effects on the commercialization of $Li-O_2$ batteries.[52-53] Cathode electrodes made from natural wood have been utilized in $Li-O_2$ batteries.[54-55] As far as reported, the electrode made from activated tea leaves is firstly used in $Li-O_2$ batteries though tea leaves have been widely employed to fabricate supercapacitor electrodes.[45, 56] We decide to test the activated tea leaves electrode at a commonly used current density of 0.1 mA/cm^2. As shown in Figure 7, the discharge capacity of activated tea leaves based electrode is ~3.0 Ah/g. When mixing

activated tea leaves and acetylene black together, both mixture_4 and mixture_5 electrodes achieve much higher discharge capacities than the electrodes coated only by the activated tea leaves. For instance, the discharge capacity of the mixture_5 electrode is about 4.7 Ah/g which is 47% higher than that of the activated tea leaves electrode. The practical use of activated tea leaves is validated and the increase in discharge capacity resulted from mixing carbons confirms the observation in Figure 6. The mixture of carbons having different specific surface area can improve the porous structure and enhance the discharge performance. Afterward, the electrode coated by activated tea leaves are discharged at 0.5 mA/cm^2 and the discharge capacity is only 1.05 Ah/g. Results in Figure 8 prove that larger specific surface area cannot help to achieve higher discharge capacity because micropores are unable to accommodate Li_2O_2. This observation agrees well with results shown in Figure 5. There are enormous environmental and economical benefits to manufacture electrodes from recycled tea leaves instead of the commercial carbons. Therefore, mixing the tea carbon and acetylene black carbon together can both increase the discharge capacity and reduce the cost of fabrication. However, the optimized weight ratio between the tea carbon and the acetylene black still need to be investigated in future research.

4. Conclusion

In summary, we fabricated electrodes using three commercial carbons and carbon made from activated tea leaves for Li−O_2 batteries. N_2 adsorption/desorption technique was employed to characterize all carbon materials. Activated tea leaves made by activating waste tea leaves had a high surface of 2868 m^2/g, most of which result from large amounts of micropores. Vulcan XC 72 (264.1 m^2/g) had more specific surface area than acetylene black (76.5 m^2/g) and Super P (60.9 m^2/g).

When electrodes made from a single type of commercial carbons were discharged at 0.5 mA/cm^2, similar discharge capacities were obtained. This indicated that a larger specific surface area may not able to result in higher discharge capacity. Micropores can result in higher surface but cannot directly enhance the discharge performance. Mixing two different carbons (e.g., acetylene black and Vulcan XC 72) increased the discharge capacity by 42% (from 2.73 ± 0.46 to 3.88 ± 0.22 Ah/g) as the mass fraction of the Vulcan XC 72 increased from 0 to 0.3. Furthermore, an electrode made from activated tea leaves was firstly demonstrated in Li−O_2 batteries after achieving the discharge capacity of ~3.0 Ah/g at 0.1 mA/cm^2. Mixtures of acetylene black and activated tea leaves verified

that the use of mixed carbons having two different specific surface areas could increase the discharge capacity. This was due to a more effective use of the mesoporous specific surface area. In addition, the electrode with activated tea leaves was discharged at 0.5 mA/cm^2 but only obtained ~1.0 Ah/g discharge capacity. This result confirmed that the discharge capacity was not proportional to the specific surface area. In conclusion, this study can provide a practical way to increase the discharge capacity using mixed carbon materials. New eco-friendly materials of activated tea leaves can reduce the cost of fabricating electrodes, and facilitate the commercialization of $Li-O_2$ batteries.

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Figure Captions

Figure 1. The schematic of the Li−O_2 battery.[47-48]

Figure 2. Results of (a) BET specific surface area, (b) BJH pore size distribution of different carbon samples except for Tea carbon and (c) BJH pore size distribution of Tea carbon.

Figure 3. Isotherms of different carbon samples.

Figure 4. SEM images of different carbon samples.

Figure 5. Discharge capacities of Li−O_2 batteries with electrodes coated by commercial carbons at 0.5 mA/cm^2.

Figure 6. Discharge capacities of Li−O_2 batteries with electrodes coated by acetylene black, mixture_1, mixture_2, and mixture_3 at 0.5 mA/cm^2. (Mixture_1: 90% Acetylene black + 10% Vulcan XC 72; Mixture_2: 80% Acetylene black + 20% Vulcan XC 72; Mixture_3: 70% Acetylene black + 30% Vulcan XC 72.)

Figure 7. Discharge curves of Li−O_2 batteries with activated tea leaves electrodes and mixtures at 0.1 mA/cm^2.

Figure 8. Discharge curves of Li−O_2 batteries with activated tea leaves electrodes and commercial carbon electrodes at 0.5 mA/cm^2.