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Hybrid Air-Electrode for Li/Air Batteries

Jie Xiao, Wu Xu,[*] Deyu Wang,[**] and Ji-Guang Zhang[*,z]

Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, USA

A hybrid air-electrode is designed to improve the energy density of Li/air batteries operating in an ambient environment. Three lithium insertion materials, MnO_2, V_2O_5, and CF_x (x = 1.0–1.15), are mixed with activated carbon to prepare different hybrid air-electrodes used in Li/air batteries. When compared with pure carbon-based Li/air batteries, the batteries using hybrid air-electrodes demonstrate significantly improved specific capacities and energies, especially for the CF_x-based hybrid Li/air batteries. Extremely hydrophobic CF_x also facilitates the formation of air-flow channels in the carbon matrix and alleviates air-electrode blocking problem during the discharge process. These hybrid air-electrodes provide a promising approach to improve the energy density of Li/air batteries.
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Recently, Li/air batteries have attracted much attention because of their high theoretical specific energy of 11,972 Wh/kg.[1,2] Unlike conventional lithium and lithium ion batteries, the cathode material of Li/air batteries (oxygen) is not stored inside the batteries. Instead, it is absorbed by the air-electrode during discharge.

Although much progress has been made since Abraham and Jiang[1] first reported on Li/air batteries that used a nonaqueous electrolyte, significant barriers still exist for the practical application of Li/air batteries operated in an ambient environment. A significant problem with Li/air batteries is that the reaction products (Li_2O and Li_2O_2) deposited in the air-electrode eventually block the oxygen flow path in the electrode[3-5] and thus reduce the number of active reaction sites. This problem (simply stated as the higher the discharge rate, the faster the fading rate of the capacity) is the main reason that the discharge rate of Li/air batteries is normally much lower than that of lithium/ion batteries. The choice of electrolyte also plays a key role on the performance of Li/air batteries.[5,6] In this regard, the viscosity, oxygen solubility, and ionic conductivity of the electrolyte are important factors. In addition, the contact angle between the electrolyte and electrode surface significantly affects the performance of Li/air batteries.[6,7] Other factors affecting the performance of Li/air batteries include the amount of the electrolyte, the selection of carbon sources,[8,9] catalyst,[10] and binder, and the thickness of the air-electrode.[11,12] If the battery needs to be operated in an ambient environment, a water diffusion barrier is required to minimize water diffusion while allowing enough oxygen to flow into the batteries for the given discharge current.

Considering the significant challenges on the practical application of Li/air batteries, we developed an approach for improving the discharge rate of Li/air batteries. This approach combines the advantages of both conventional lithium ion batteries and Li/air batteries. Three different hybrid air-electrodes composed of a mixture of active carbon and three ion insertion materials (MnO_2, V_2O_5, or CF_x) were prepared and used in Li/air batteries. The electrochemical performances of the conventional Li/air batteries, lithium batteries, and the hybrid Li/air batteries are compared in this paper.

Experimental

Three lithium insertion materials were used in hybrid air-electrodes. MnO_2 was provided by Enerize Corp. V_2O_5 was obtained by thermal decomposition of NH_4VO_3 (Aldrich) at 500°C in air for 3 h. CF_x (x = 1–1.15) was acquired from Advance Research Chemicals, Inc. The crystal structures were characterized at room temperature using a Philips Xpert X-ray diffractometer in θ-2θ scan mode and Cu Kα radiation at λ = 1.54 Å.

The air-electrodes for Li/air batteries were prepared by mixing active carbon Ketjenblack, referred to as KB hereafter (EC600JD, Akzo Nobel), with DuPont Teflon poly(tetrafluoroethylene) (PTFE)-TE3859 fluoropolymer resin aqueous dispersion (60 wt % solids). For the regular air-electrode, the carbon Teflon weight ratio (after drying) was 85:15. The final loading of carbon in the electrode was 15.1 mg/cm^2. For the hybrid electrode, the carbon:lithium insertion material:PTFE weight ratio was 55:30:15. Therefore, in each hybrid electrode, the total percentage of carbon and lithium insertion material was always 85%. The air-electrode films were formed by passing dry powder of the above mixtures through a stainless steel colander with 80 psi pressure. The final loadings of the MnO_2/KB-, V_2O_5/KB-, and CF_x/KB-based hybrid air-electrodes were 25.2 mg (MnO_2 + KB)/cm^2, 17.9 mg (V_2O + KB)/cm^2, and 22.4 mg (CF_x + KB)/cm^2, respectively. Nickel mesh (29.6 mg/cm^2, Gerard Daniel Worldwide) was laminated with the air-electrodes described above and served as the current collector. To minimize moisture diffusion and to facilitate gas distribution, a porous Teflon film (3 mil thick, Gurley number is 30 s, 67% porosity, and the density is 0.66 g/cm^3, W.L. Gore and Associates, Inc.) was laminated on the outside of the electrode exposed to the air. Circular electrode disks (1.98 cm^2 in area) with a 2 mm nickel tab on the edge were punched from the air-electrode. The schematic structure of the hybrid Li/air battery is shown in Fig. 1. As a comparison, lithium metal batteries (Li/MnO_2, Li/V_2O_5, and Li/CF_x) were prepared by mixing the lithium insertion materials with super P (from Timcal) and poly(vinylidene fluoride) (KYNAR HSV900 from Arkema Inc.) in a weight ratio of 80:10:10. 1-Methyl-2-pyrrolidinone (Aldrich) was used as the solvent. The slurries were cast on an aluminum foil and dried at 65°C. The electrodes were punched into circular disks (~1.4 cm diameter) with an active material loading of typically 10 mg/cm^2.

The Li/air coin cells (type 2325 coin cell kits from CNRC, Canada) were assembled in an argon-filled glove box (MBraun Inc.) with moisture and oxygen content of less than 1 ppm. The positive pans of the kits were machine-drilled 19 × ⌀ 1.0 mm holes that were evenly distributed on the pans to allow air passage. The small tab on the circular electrode was spot welded onto the positive pan to allow the flow of electrons. Lithium disks (1.59 cm diameter and 0.5 mm thick) were used as the anode. The electrolyte was optimized[11] and prepared by dissolving 1 mol lithium bis(trifluoromethanesulfonyl)imide (battery grade, Ferro) in ethylene carbonate/propylene carbonate (1:1 weight ratio). The salts and solvents used in the electrolyte were all battery grade materials from Ferro Corp. A Whatman GF/D glass microfiber filter paper (~1.9 cm diameter) was used as the separator because it holds more electrolyte than most polymer-based separators. The coin cells were placed in a glove box filled with dry air to minimize the influence of moisture. The glove box had a gas inlet and an outlet so the interior pressure was kept positive by allowing the dry air to flow through continuously. The humidity inside the glove box was less than 1% relative humidity measured by a Dickson handheld

* Electrochemical Society Active Member.
** Electrochemical Society Student Member.
z E-mail: jiguang.zhang@pnl.gov

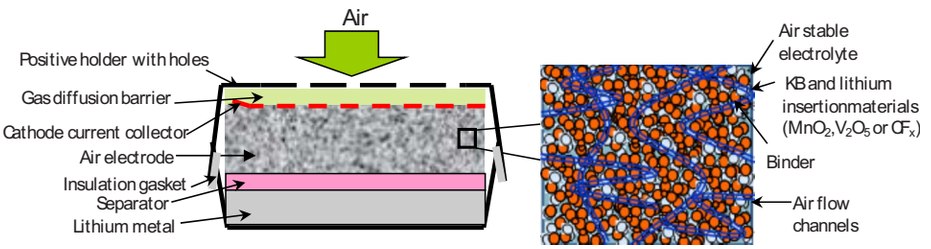

Figure 1. (Color online) Schematic of a Li/air hybrid battery based on coin cell design.

temperature/humidity/dew point monitor. The electrochemical tests were performed at room temperature in an Arbin BT-2000 battery tester. Unless otherwise specified, the cells were discharged at a current density of 0.05 mA/cm^2 to 2.0 V and then held at 2.0 V until the current density decreased to less than $I/5 = 0.01$ mA/cm^2. The capacities reported here are normalized to per gram of carbon or per gram of total active material (including carbon and the other lithium insertion material) in the electrodes.

Results and Discussion

The X-ray diffraction (XRD) patterns of KB, MnO_2, V_2O_5, and CF_x are shown in Fig. 2. V_2O_5 was obtained by heating NH_4VO_3 at 500°C for 3 h in air. The decomposition product crystallized in a typical orthorhombic structure that indicated a pure phase of V_2O_5. The XRD pattern of MnO_2 shown in Fig. 2 is the most common γ-MnO_2, which is an intergrowth between rutile MnO_2 (β-MnO_2) and ramsdellite MnO_2 (R-MnO_2). The KB and CF_x shown in Fig. 2a and d are mainly amorphous.

The electrochemical reactions for each lithium insertion material during the discharge process are shown below

$$MnO_2 + Li \rightarrow LiMnO_2 \quad [1]$$

$$V_2O_5 + xLi \rightarrow Li_xV_2O_5 \quad (x \approx 3) \quad [2]$$

$$CF_x + xLi \rightarrow C + xLiF \quad (x = 1.0\text{–}1.15) \quad [3]$$

We investigated the electrochemical performances of pure MnO_2, V_2O_5, and CF_x in primary lithium batteries as references. The voltages as a function of the specific capacities of these materials are plotted in Fig. 3. Although the specific capacity from pure MnO_2 is only 233 mAh/g at a C/20 rate, MnO_2 was selected as a candidate to prepare the hybrid air-electrode because of its catalytic effect.[13] The discharge plateau of the pure MnO_2 cathode occurs at about 2.8 V, which is similar to that of the KB-based Li/air battery discharged at a low current density ($I = 0.05$ mA/cm^2).[12] For the V_2O_5 cathode, several different discharge plateaus are observed, with the first two occurring at about 3.3 and 2.3 V, respectively. The third plateau overlaps with the constant voltage part at 2.0 V. This discharge profile provides additional capacity to those of the lithium/oxygen in Li/air batteries. The specific capacity of the as-prepared V_2O_5 alone is 370 mAh/g, much higher than that of MnO_2 at a current density of 0.1 mA/cm^2. CF_x was selected as a good candidate for the hybrid air-electrode because of its high theoretical specific capacity.[14] At a C/10 rate (~86 mA/g corresponding to the current density of 0.3 mA/cm^2), the discharge capacity of CF_x reaches approximately 850 mAh/g. However, because of the poor electronic conductivity and the slow kinetics of the cell reaction between Li and CF_x, an initial voltage delay is very common in Li/CF_x cells especially when $x \geq 1$.[14] The operation voltage is relatively low (2.3–2.4 V) in the CF_x primary battery, as shown in Fig. 3.

Different hybrid air-electrodes using a mixture of the lithium ion insertion materials and KB as described above were used in the Li/air batteries and tested in a dry air environment. The discharge voltages as a function of specific capacity of these batteries are compared in Fig. 4. For a conventional air-electrode based on KB carbon without lithium ion insertion materials, the discharge capacity is usually high (above 1700 mAh/g) at a low current density (such as 0.05 mA/cm^2).[12] However, when the current density is increased to 0.1 mA/cm^2, the specific capacity of the air-electrode decreases rapidly to approximately 432 mAh/g and to approximately 300 mAh/g at discharge rates of 0.1 and 0.2 mAh/g, as shown in Fig. 4a and b, respectively. At high discharge rates, the pore structure of the air-electrode is quickly blocked by the reaction product (Li_2O_2 and Li_2O). The inner layer of the air-electrode then becomes inaccessible to oxygen so the battery capacity significantly decreases. In this case, a high discharge capacity for the air-electrode can only be achieved at a very low discharge rate.

When 30% MnO_2 is added to the air-electrode, the discharge

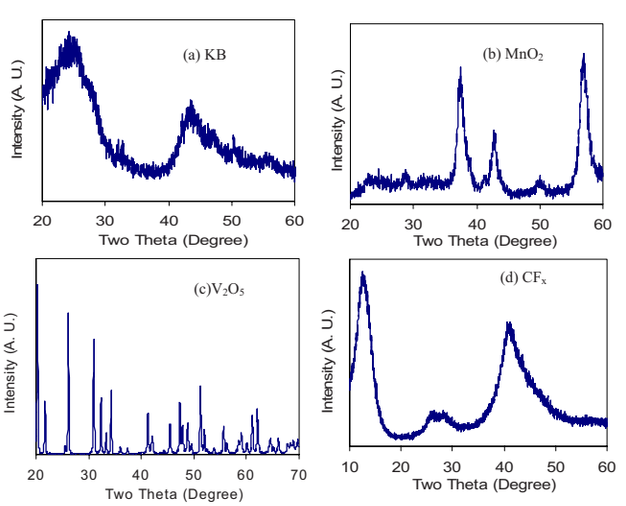

Figure 2. (Color online) XRD patterns of (a) pure KB, (b) MnO_2, (c) V_2O_5, and (d) CF_x.

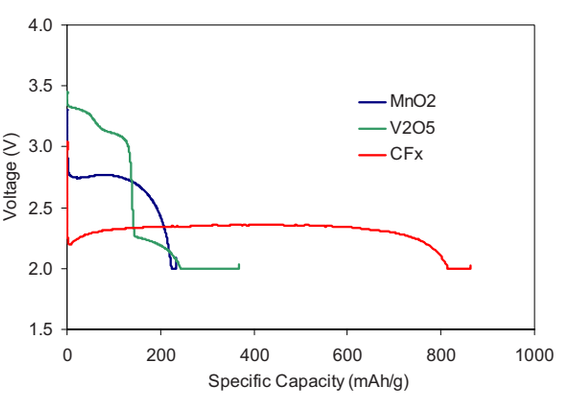

Figure 3. (Color online) Voltages as a function of specific capacities for different lithium batteries. MnO_2 was discharged at a C/20 rate (11 mA/g), V_2O_5 was discharged at a C/13 rate (28 mA/g), and CF_x was discharged at a C/10 rate (86 mA/g).

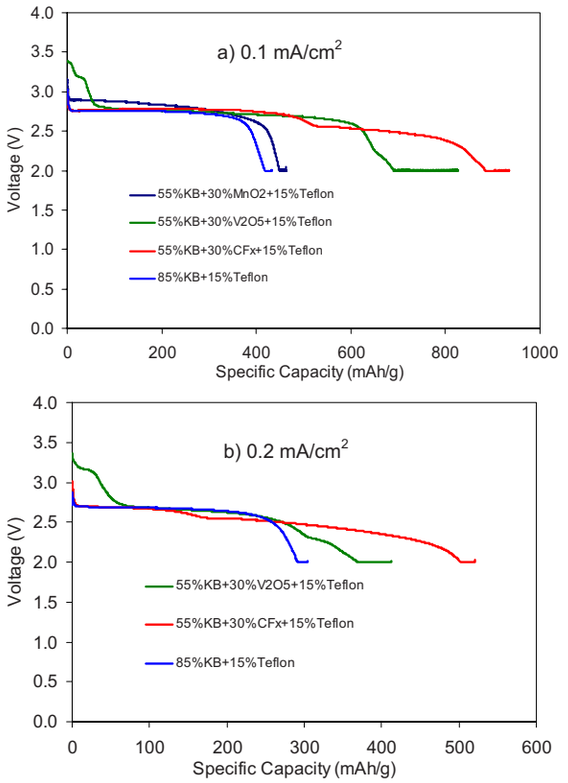

Figure 4. (Color online) Hybrid Li/air batteries discharged at different rates: (a) 0.1 and (b) 0.2 mA/cm^2. All the batteries were tested in dry air at ambient pressure (oxygen partial pressure = 0.21 atm). Capacities are expressed as per gram of total active mixtures in the air-electrode.

capacity of the battery shows only a slight improvement with a single operation voltage of 2.7–2.8 V, as shown in Fig. 4. In fact, the discharge curve for a Li/air battery using a MnO_2/KB-based hybrid air-electrode is very similar to that of a pure KB-based Li/air battery at 0.1 mA/cm^2. No obvious catalytic effect is observed from MnO_2 in this hybrid battery even though the proportion of MnO_2 used in the electrode mixture is as high as 30%. Instead, MnO_2 mainly works as an intercalation host for lithium in the air-electrode. Although several groups[10,15] reported increased capacities in both the primary and rechargeable Li/air batteries by using an MnO_2-based catalyst, no significant improvement was observed on the capacity of Li/air batteries using the γ-MnO_2/KB-based hybrid air-electrode. This apparent difference can be attributed to several reasons. One reason is that the structure and morphology of the γ-MnO_2 used in this work may have less catalyst effect than α-MnO_2 nanowires used in the previous report.[15] Another possible reason is that the catalyst used in low oxygen partial pressure (0.21 atm) may be less effective than those used in the pure oxygen environment (>1 atm).[10,15] Therefore, nano-MnO_2/KB-based hybrid air-electrode is not further evaluated at higher discharge rates.

For the V_2O_5/KB-based hybrid air-electrode, a significant improvement in the specific capacity at a higher discharge rate was observed, as shown in Fig. 4. The specific capacity of the V_2O_5/KB hybrid air-electrode is more than twice that of the pure KB-based Li/air battery at a current density of 0.1 mA/cm^2. The characteristic plateaus for pure V_2O_5 and KB continuously appear in the discharge process, exhibiting a very good combination of different electrochemical reactions. Even at a current density of 0.2 mA/cm^2, a specific capacity of more than 400 mAh/g is obtained in the V_2O_5/KB hybrid air-electrode. Considering the high specific capacity and good reversibility of the V_2O_5 cathode when used in rechargeable lithium ion batteries, the V_2O_5/KB-based hybrid air-electrode can be a good candidate for rechargeable Li/air batteries.

The advantage of the hybrid air-electrode is well illustrated in Li/air batteries using a CF_x/KB hybrid air-electrode, as shown in Fig. 4. Two distinct plateaus were observed in this case. The first plateau corresponds to the reaction between lithium and oxygen, whereas the second plateau corresponds to the lithium reaction with carbon monofluoride ($CF_x + xLi = C + xLiF$). This phenomenon can be explained as follows: During the low rate discharge process, the lithium–oxygen reaction ($2Li + O_2 = Li_2O_2$ and $4Li + O_2 = 2Li_2O$) first occurs at 2.7–2.8 V. Because of the presence of the extremely hydrophobic CF_x in this hybrid structure, extra air flow channels were provided in the air-electrode, as shown in Fig. 1. More interior carbon can be utilized in the CF_x/KB hybrid air-electrode, and the effect of electrode blocking (by reaction products Li_2O_2/Li_2O) can be reduced, especially at a high discharge rate. As active reaction sites are exhausted and the reaction products Li_2O_2 and Li_2O gradually block the air-electrode, the cell resistance begins to increase and the cell voltage begins to decrease. When the cell voltage drops to the voltage plateau of the lithium ion insertion reaction in CF_x, the lithium ions begin to react with CF_x, and the voltage is stabilized at this voltage until all the CF_x has been reacted.

The plateau corresponding to the reaction between lithium and CF_x (see Fig. 4) occurs at 2.5 V, which is a slightly higher voltage than in that observed for the reaction in a conventional CF_x primary battery (see Fig. 3). This increased cell voltage or reduced polarity can be attributed to the fact that a much larger portion of conductive carbon was used in the hybrid air-electrode (KB:CF_x = 50:30) than was used in lithium/CF_x batteries (super P:CF_x = 10:80).

Another advantage of this CF_x/KB hybrid air-electrode is that its configuration can avoid the voltage delay effect normally observed in pure CF_x primary batteries. Thus, this combination of Li/air and lithium/CF_x batteries also provides a physical approach in eliminating the initial voltage delay that is a characteristic of Li/CF_x batteries.[14,16] The specific capacities of the CF_x/KB hybrid cell reached 935 and 521 mAh/g at current densities of 0.1 and 0.2 mA/cm^2, respectively. These values are much larger than those of conventional Li/air batteries obtained under similar discharge conditions (approximately 400 and 300 mAh/g active materials at current densities of 0.1 and 0.2 mA/cm^2, respectively). More importantly, when the total weight of a battery is considered, Li/air batteries with CF_x/KB hybrid air-electrodes exhibit higher specific energies than Li/air batteries using conventional KB air-electrodes and lithium/CF_x primary batteries. Our data on pouch cells, which will be published later,[17] confirm this conclusion. Therefore, the hybrid electrode provides an efficient approach for improving the rate capability of Li/air batteries especially at low to moderate current densities.

The specific energies of these Li/air batteries are compared in Fig. 5. The improvement in the specific energy from the hybrid air-electrode can be placed in the following order: CF_x/KB > V_2O_5/KB > MnO_2/KB > KB. In the CF_x/KB air-electrode, CF_x particles are extremely hydrophobic. This unique property may further facilitate air transport in the carbon-based air-electrode. The CF_x:KB ratio can be tailored to satisfy different trade-offs between discharge capacity and discharge rate for specific applications.

Conclusions

We have developed an approach that can significantly improve the specific energy of Li/air batteries. Three kinds of hybrid air-electrodes based on MnO_2/KB, V_2O_5/KB, and CF_x/KB were evaluated at current densities of 0.1 and 0.2 mA/cm^2. For the MnO_2/KB air-electrode, the catalyst effect from the commercial MnO_2 is not significant, and MnO_2 mainly works as a lithium insertion material with a similar discharge plateau as that of the Li/air battery. The Li/air battery using the V_2O_5/KB-based hybrid air-electrode exhibits several distinct voltage plateaus and has a specific capacity greater than 800 mAh/g at a current density of 0.1 mA/cm^2, which is twice

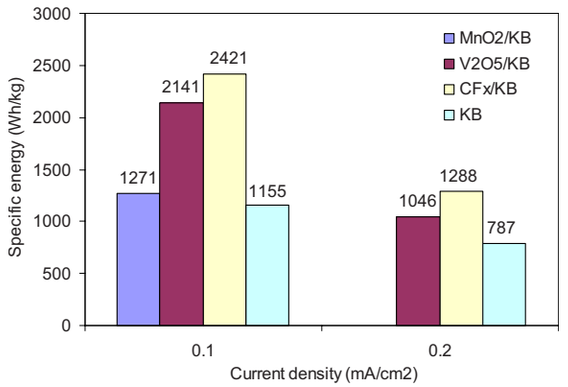

Figure 5. (Color online) Comparison of the specific energies for different Li/air hybrid batteries at a discharge current density of 0.1 mA/cm^2 and a current density of 0.2 mA/cm^2.

as large as those of pure KB-based Li/air batteries tested under the similar conditions. The advantage of this hybrid battery design is more pronounced in CF_x/KB hybrid cells in which high discharge capacities of 950 and 521 mAh/g can be achieved at current densities of 0.1 and 0.2 mA/cm^2, respectively. The high theoretical capacity, rate capability, and hydrophobic property of CF_x enhance the electrochemical performance of a conventional air-electrode based on pure active carbon; the combination of KB, however, also improves the conductivity and utilization of CF_x. The CF_x:KB weight ratio in the air-electrode can be tailored to satisfy the specific capacity and energy density requirements for different applications.

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