Energy &
Environmental Science

Cite this: *Energy Environ. Sci.*, 2011, **4**, 4994

www.rsc.org/ees

PAPER

A lithium–air capacitor–battery based on a hybrid electrolyte†

Yonggang Wang, Ping He and Haoshen Zhou*

Received 12th July 2011, Accepted 9th September 2011
DOI: 10.1039/c1ee02121d

A hybrid electrolyte lithium–air battery, in which a lithium-anode in a non-aqueous electrolyte and an air catalytic cathode in an aqueous electrolyte solution were separated by a ceramic LISICON film, has been investigated in our previous work. In the present work, a capacitor electrode was put in the non-aqueous electrolyte solution as an additional cathode in parallel with the air catalytic cathode. The proposed lithium–air batteries with an additional capacitor cathode can successfully unite capacitor character and lithium–air battery character in one device which is now nominated as a "lithium–air capacitor–battery based on a hybrid electrolyte". When high power is needed, the capacitor cathode would play the main role of peak power output; when high energy is demanded, the air catalytic cathode would display its high energy character. The adjustability of power output and energy output demonstrate that the proposed lithium–air capacitor–battery should be a promising power system for future electric vehicles.

Introduction

Facing the serious emission of CO_2 gases arising from petroleum-based transportation and the limited storage of fossil energy, it has been a world topic to realize a low carbon society which is based on hybrid electric vehicles (HEVs) and electric vehicles (EVs).[1] Nowadays, the lithium-ion battery has been considered as the most suitable power source for EVs (or HEVs), because of its higher energy density compared with other rechargeable batteries, such as Lead–Acid and Ni–MH. However, for the future time of EVs, present lithium-ion battery technology is still facing the great challenge. In Japan, the final target of the New Energy and Industrial Technology Development Organization (NEDO) project for batteries in next-generation EVs is to develop a battery with a high energy density of 700 Wh kg^{-1}, which is comparable with the energy density of a conventional internal combustion engine. Unfortunately, the typical energy density of today's lithium-ion battery is just between 100–200 Wh kg^{-1}, which is far away from the final target of the NEDO project.[2] Thereby, many efforts are being made to develop the next generation lithium-ion battery with a large capacity, which is also called a post-lithium-ion battery.

In recent two years, the lithium–air battery has attracted worldwide attention as a possible power system for future EVs, owing to its super-large theoretical energy density.[1,3] An oxygen cathode proceeding in tandem with a lithium-anode according to the reaction $2Li + O_2 \rightarrow Li_2O_2$, which includes a cathodic reaction of $2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$ and an anodic reaction of

Broader context

It has become an urgent challenge to build a low carbon society against the global warming resulting from serious CO_2 emission for human beings. The key technology for the challenge is to develop a hybrid electronic vehicle (HEV) and/or electronic vehicle (EV) based on high energy rechargeable lithium ion batteries. However, although intense efforts are paid worldwide to design and synthesize new intercalation compounds with higher capacity, the energy density of lithium ion batteries is still limited by the low capacity of the positive electrode. Recently, the lithium–air battery has attracted worldwide attention as a possible post lithium ion battery because of its super-large theoretical energy density. However, the power performance of a hybrid electrolyte based lithium–air battery is much limited by the low diffusion rate of O_2 within porous air catalytic electrodes and the poor conductivity of the hybrid electrolyte in various lithium air batteries, which can't satisfy the high power demand from future HEVs or EVs.
In the present work, we developed a hybrid electrolyte lithium–air capacitor–battery by adding an additional capacitor electrode inside the lithium air battery. This lithium–air capacitor–battery can achieve high peak power or high energy density according to various operating conditions and application demands.

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, 305-8568, Japan. E-mail: hs.zhou@aist.go.jp; Fax: +81-29-861-3489; Tel: +81-29-861-5795

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1ee02121d

$2Li - 2e^- \rightarrow 2Li^+$, can deliver an energy density of 3600 Wh kg^{-1} (= (capacity of 1200 Ah kg^{-1}) × (operating voltage of 3.0 V)).[1] Herein, the theoretical energy density (3600 Wh kg^{-1}) is based on the total mass of oxygen and lithium. If the inexhaustible oxygen from air can be directly utilized, a lithium–air system would display higher energy density. The first lithium–air battery, with a structure of Li/organic electrolyte/air, was successfully assembled and investigated in 1996.[4] However, this work did not capture wide attention until Bruce *et al.* demonstrated its rechargeable ability recently.[5] Then, the lithium–air battery attracted wide attention.[3,6–20] However, the combination of lithium and oxygen for electric energy generation is also a great challenge, because water and O_2 dissolved in the organic could directly oxidize the lithium by chemical reaction. The direct contact between O_2 and organic electrolyte results in serious decomposition of the organic solvent.[21] Furthermore, the discharge product Li_2O_2 is not soluble in the organic electrolyte, and gradually clogs the porous air electrode.

In 2007, Polyplus Battery Company united a ceramic electrolyte protected lithium-electrode with Pt-catalyzed O_2 reduction in aqueous solution to form a lithium–air battery.[22] The ceramic protection layer is a lithium superionic conductor film (LISICON, it is a kind of Li-ion conducting film), which only permits the passage of Li^+. Recently, our group employed a LISICON thin-film to separate a lithium-anode in an organic electrolyte and an oxygen-cathode in an aqueous electrolyte, and proposed a lithium–air battery. This kind of lithium–air system is named as a hybrid electrolyte lithium–air battery.[23–28] Owing to the oxygen reduction product (OH^-) being soluble in aqueous solution, the hybrid electrolyte lithium–air battery can continuously reduce the oxygen from air to deliver energy, just like a fuel cell. In the hybrid electrolyte lithium–air battery, the lithium-anode would not be oxidized by O_2 or water because of the ceramic protection layer. In addition, the incombustible aqueous electrolyte would avoid the unsafe problem of battery burning. However, the power performance of the hybrid electrolyte lithium–air battery is much limited by the low diffusion rate of O_2 within the porous air catalytic electrode and poor conductivity of the ceramic electrolyte (LISICON), which can not reach the high power demand for future HEVs or EVs. Thereby, it is the next logical step to further improve the power performance of the hybrid electrolyte lithium–air battery.

In the present work, we developed a hybrid electrolyte lithium–air battery with an additional capacitor electrode. Here, introducing a super-capacitor cathode electrode into the hybrid electrolyte inside of the Li–air battery system is a new concept. In fact, only the Li–air battery based on the hybrid electrolyte could be used for this investigation because this Li–air battery can provide a relatively stable charge–discharge cycle performance.[28] However, the Li–air battery based on non-aqueous electrolytes can't provide a stable charge–discharge cycle performance until now because there are some problems from decomposition of the non-aqueous electrolyte in both the charge and discharge processes.[29] This novel energy conversion system can achieve high peak power or high energy density based on various operating conditions and application demands. When discharged by a large current, the proposed energy conversion system displays the character of a supercapacitor, and delivers large peak power; when operated with a low current, it exhibits the character of a lithium–air battery, and delivers high energy density. The proposed energy conversion system may provide a new development direction for future lithium–air capacitor–batteries.

Results and discussion

Structure and operating principle of the lithium–air capacitor–battery based on a hybrid electrolyte

The structure of the proposed lithium–air capacitor–battery based on a hybrid electrolyte is shown schematically in Fig. 1, where the organic electrolyte (1 M $LiClO_4$ in EC/DCE) and the aqueous electrolyte (1 M KOH) are separated by a water stable ceramic LISICON film. A porous air catalytic electrode in aqueous solution serves as the cathode. Metallic lithium film in the organic electrolyte is used as the anode. As shown in Fig. 1, an activated carbon based capacitor electrode is employed in the organic electrolyte as added cathode. Furthermore, the activated carbon based electrode and the porous air catalytic electrode are connected together. Summarily, the proposed system can be explained as: a lithium–air battery in parallel with a lithium-activated carbon capacitor.

As mentioned in the introduction, the proposed lithium–air battery with an additional capacitor electrode can display the character of a supercapacitor or the character of a lithium–air battery with the variation of various application demands and operating conditions, and can be called a lithium–air capacitor–battery. Herein, we take the operation of an EV as an example to simply introduce the various demands for the battery system, and then briefly analyze the operating principle of the proposed lithium–air capacitor–battery under different operating conditions. Generally, the operating of an EV can be roughly divided

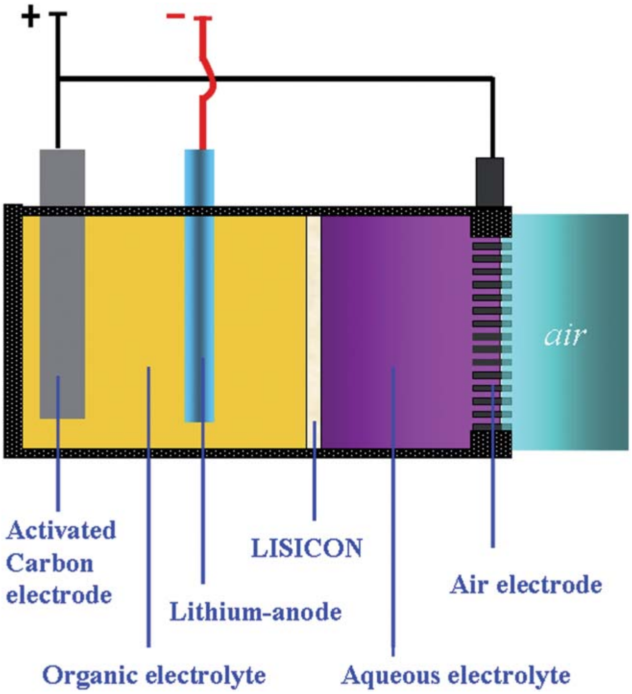

Fig. 1 A schematic structure representation of the lithium–air capacitor–battery based on a hybrid electrolyte.

into three stages: 1) operating with a constant speed. During this process, the battery system of an EV should provide a low and stable power for long-time; 2) accelerating operating process. On this process, the battery system for an EV should provide a high peak power in a short time; 3) decelerating operating process and constant speed operating process after accelerating process. For this process, the battery system for an EV could reduce or stop power output. According to the various operation conditions mentioned above, we further analyzed the operating principle of our proposed lithium–air capacitor–battery at different stages. 1) Discharge with a stable low current. On this process the operating principle of the proposed lithium–air capacitor–battery based on a hybrid electrolyte is shown schematically in Fig. 2a. In the porous air catalytic electrode, the O_2 obtains electrons from out circuit and is converted in to OH^-; simultaneously, the capacitor electrode obtains electrons from out circuit, and adsorbs lithium-ions to deliver capacity. In parallel with the reactions that occurred in the air catalytic electrode and the capacitor electrode, metallic lithium-anode is transformed into lithium-ions. For these generated lithium-ions, some diffuse from the organic electrolyte to the aqueous electrolyte across the LISICON film, others diffuse to the surface of the additional carbon electrode. Around the external circuit, from the lithium-anode electrons flow to the air catalytic electrode and the capacitor electrode across the electric device. 2) Discharge with large current to provide high peak power. For this process, the operating principle of the proposed lithium–air capacitor–battery based on a hybrid electrolyte is given in Fig. 2b. In this situation, the proposed lithium–air capacitor–battery mainly presents the character of a supercapacitor. In other words, on the external circuit, the electron flow is mainly from the lithium-anode to the additional capacitor (or carbon) electrode. Compared with the additional capacitor, the electrons obtained by the air catalytic electrode are almost negligible. Within the proposed system, lithium-ions mainly diffuse from the lithium-anode to the additional capacitor electrode. In brief, on high discharge, the additional capacitor (or carbon) electrode plays the main role of high power output. 3) Rest or low current discharge after high power output. In the very short time after the high current discharge (or high power output), the operating potential of the air catalytic electrode should immediately recover to its initial state, whereas the operating potential of the capacitor should keep the potential at the end of the high current discharge. In other words, in the very short time after high current discharge, there is a potential difference between the air catalytic electrode and capacitor electrode. In this situation, the proposed lithium–air battery with an additional capacitor (or activated carbon) electrode could be divided into two kinds of devices, a lithium–carbon capacitor and a lithium–air battery. Owing the potential difference between the air catalytic electrode and the capacitor, the lithium–carbon capacitor should be charged by the lithium–air battery. The operating principle of the proposed lithium–air capacitor–battery based on a hybrid electrolyte in this situation is presented in Fig. 2c. As shown in Fig. 2c, the electron flow around external circuit could be negligible, such as in a rest state. The electrons flow from capacitor electrode to the air catalytic electrode. Within the porous catalytic electrode, O_2 from air couples with electrons, and is reduced into OH^-; simultaneously, desorption

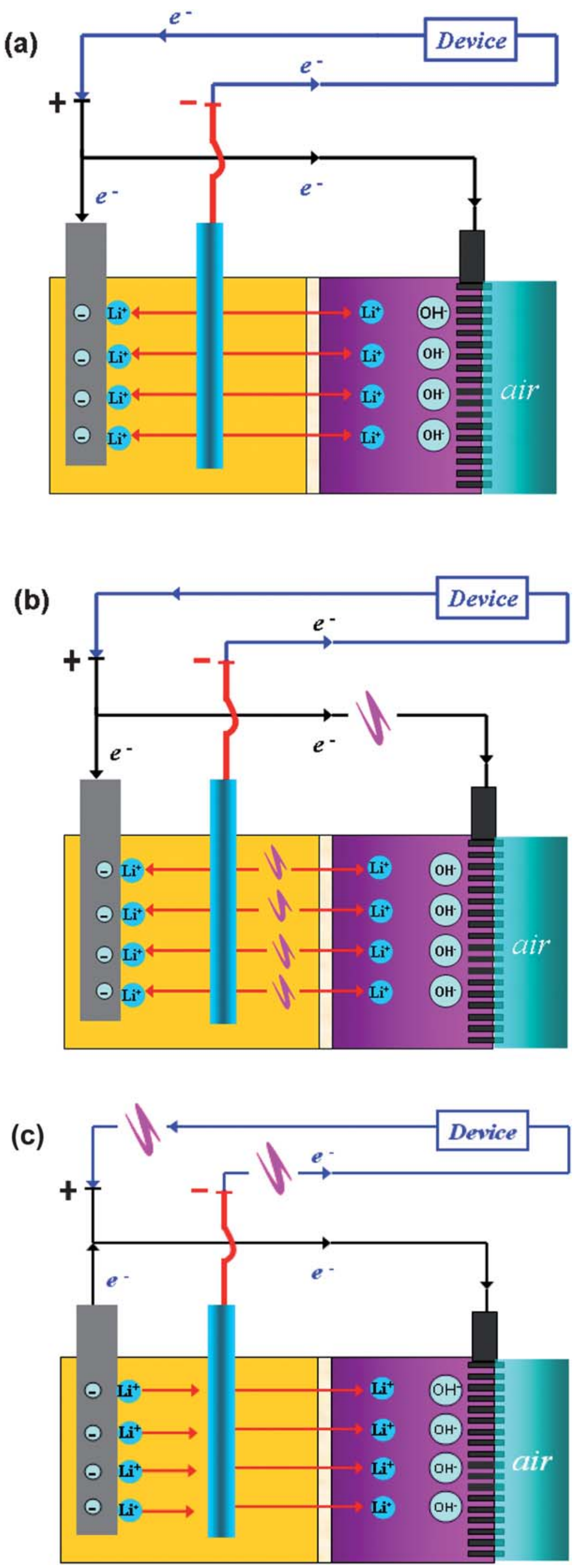

Fig. 2 A schematic showing the operating principle of the proposed lithium–air capacitor–battery based on a hybrid electrolyte at different operating conditions. (a) Discharge with low current; (b) discharge with high current; (c) rest or low current discharge after high current discharge.

of lithium-ions takes place on the surface of the capacitor electrode. Then, the formed lithium-ions diffuse from the organic electrolyte to the aqueous electrolyte.

As analyzed in Fig. 2, the operating principles of the proposed lithium–air capacitor–battery based on a hybrid electrolyte depend on the operating conditions and application demands. In the following section, we investigate the electrochemical performance of the proposed lithium–air capacitor–battery based on a hybrid electrolyte under different test conditions. Fig. 3 compares the electrochemical performance of the lithium–air capacitor–battery based on a hybrid electrolyte with that of a lithium–air battery without the capacitor electrode. As shown in Fig. 3a, with the increase of the discharge current, the lithium–air capacitor–battery displays more and more supercapacitor performance. When the applied discharge current is 1 mA (see Fig. 3a), the lithium–air capacitor–battery presents a flat discharge curve, which is similar to that of the lithium–air battery without a capacitor electrode (see Fig. 3b). As analyzed in Fig. 2a, the prepared lithium–air capacitor–battery presents the mixed character of a supercapacitor and a lithium–air battery. When the discharge current is increased to 10 mA, the lithium–air capacitor–battery displays a sloping discharge curve, which is the typical character of a supercapacitor (see Fig. 3a). However, the lithium–air battery without a capacitor electrode still has a flat discharge curve (See Fig. 3b). It should also be noted that the discharge potential (tested with a current of 10mA) of the lithium–air capacitor–battery is much higher than that of the lithium–air battery without a capacitor electrode. This result clearly demonstrates that the additional capacitor electrode can effectively improve the power output of the system. This phenomenon becomes more and more obvious with the further growth of the discharge current. For instance, at a discharge current of 100 mA, the lithium–air capacitor–battery presents totally supercapacitor performance. The initial discharge potential of the lithium–air battery with an additional capacitor is as high as 1.3 V, whereas the lithium–air battery without the capacitor electrode can not endure a current of 20 mA at all.

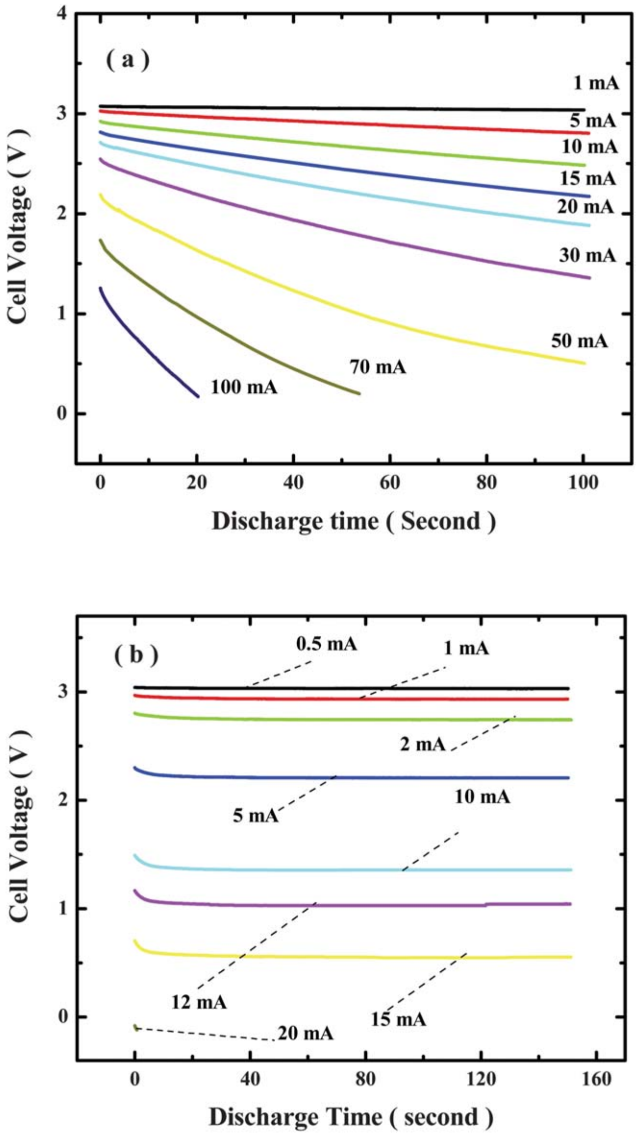

Fig. 3 Discharge curves at different currents of (a) the lithium–air capacitor–battery and (b) the lithium–air battery without a capacitor electrode.

The peak power of the lithium–air capacitor–battery and the lithium–air battery without a capacitor electrode are compared in Fig. 4. The peak power density mentioned in Fig. 4 is calculated by equation: $P = I \times V$. Where, P is the peak power (mW cm^{-2}); I is the discharge current density (mA cm^{-2}), and V is the initial voltage of discharge. As shown in Fig. 4, the maximum peak power achieved by the lithium–air capacitor–battery is almost ten times higher than that of the lithium–air battery without a capacitor electrode. The result shown in Fig. 4 further demonstrates that the additional capacitor effectively increased the power performance of the lithium–air battery.

Generally, electric devices need high peak power in a very short time, and then the battery systems for electric devices can keep a very low power output or have a rest state. In order to clarify this point, we schematically exhibit some operating

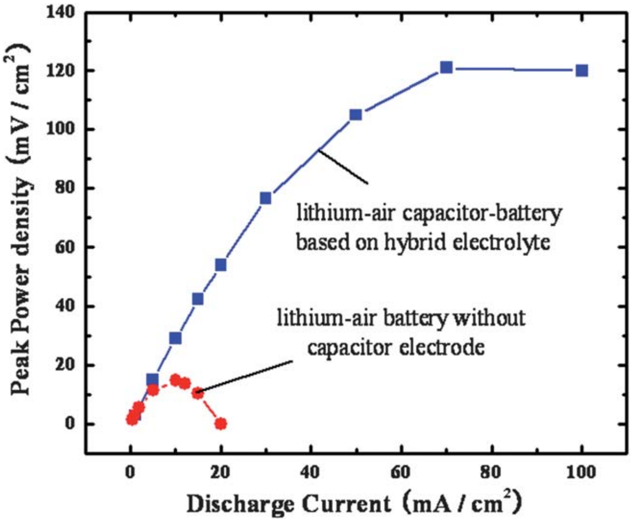

Fig. 4 A peak power density comparison between the lithium–air capacitor–battery based on a hybrid electrolyte and the lithium–air battery without a capacitor electrode.

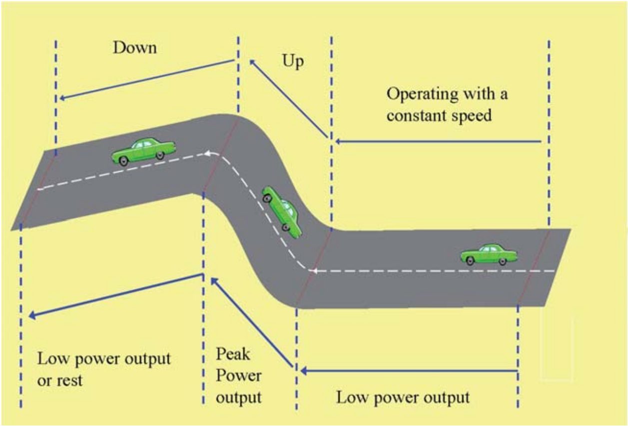

Fig. 5 A schematic showing the various operating conditions of EVs.

conditions of EVs (see Fig. 5).As shown in Fig. 5, the operating conditions of EVs can be roughly summarized as: low power output, high peak power output and rest (or low power output) after high peak power output. It should also be noted that the real operating conditions of EVs are much more complex than those shown in Fig. 5.

In Figs 3 and 4, we have investigated and discussed the electrochemical performance of the proposed lithium–air capacitor–battery based on a hybrid electrolyte at low power output (or discharge with a low current) and high peak power output (or discharge with a high current). Herein, we further test its rest state (or low power output) just after its high peak power output. The proposed lithium–air capacitor–battery based on a hybrid electrolyte was discharged with different currents, coupled with a rest step. As shown in Fig. 6, the proposed cell was discharged for several seconds and then had a 5 minute rest. It can be clearly detected that with the increase of the discharge current, the proposed lithium–air capacitor–battery based on a hybrid electrolyte displays more capacitor character – a sloping discharge curve. It is interesting that during the rest process, the cell voltage increases automatically. For example, just after the discharge with a current of 50 mA, the cell voltage recovers quickly (see the insert of Fig. 6), indicating a typical self-charge process. This can be explained by Fig. 2c. During the rest process, the electron flow around the external circuit could be negligible. The proposed lithium–air capacitor–battery can be considered as a lithium–air battery in parallel with a lithium–carbon capacitor. When the high rate discharge process is finished, the potential of the air catalytic electrode recovers its initial state (about 3.3 V), whereas the potential of the capacitor electrode remains as it was at the end of the discharge. Thereby, in a very short time just after the high current discharge process, there should be a potential difference between the air catalyst electrode and the capacitor electrode. In this situation, the lithium–carbon capacitor should be charged by the lithium–air battery. Herein, we call it a self-charge process. During the self-charge process (see Fig. 2c), the electrons flow from the capacitor electrode to the air catalytic electrode. Within the air catalyst electrode, O_2 from air is reduced into OH^- after coupling electrons from the capacitor electrode with desorbing lithium-ions from the surface of the capacitor electrode. Then, these desorbed lithium-ions diffuse from the organic electrolyte to the aqueous electrolyte. It should also be noted that with a high discharge rate, the voltage only partially recovers even after the post-rest step (Fig.6). In future study, it is necessary to further improve the conductivity of the LISICON film and optimize the mass or area ratio of the capacitor electrode to the air electrode (see ESI†). Certainly, if a longer rest step was applied, the device would be self-charged to the initial cell voltage (3.3 V).

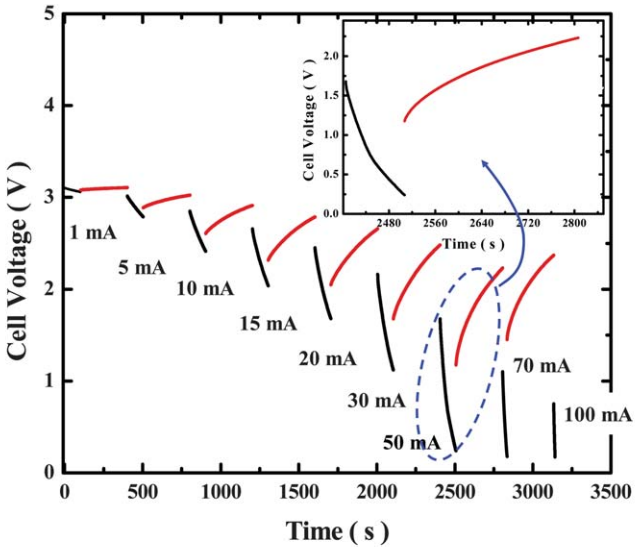

Fig. 6 Cell voltage *vs.* operating time (the lithium–air capacitor–battery based on a hybrid electrolyte was discharged with different currents, coupled with a rest step). Black line: voltage variation during discharge process; red line: voltage variation during rest process.

Summarily, the results achieved in the present work demonstrate that the lithium–air capacitor–battery based on a hybrid electrolyte is a promising power system for future EVs. Moreover, it is suitable not only for EVs but also for electric storage systems based on a smart grid. The developing history of energy storage/conversation devices has clearly demonstrated that it is almost impossible to achieve both high power density and high energy density within a single device. For instance, a hydrogen fuel cell (H_2–O_2 FC) or a lithium–air battery has super-high energy density, whereas they display very poor power performance. On the contrary, a super capacitor has very high power performance. However, its energy density is much lower because of the limited surface energy storage. Compared with a H_2–O_2 FC and a supercapacitor, the current lithium-ion capacitor–battery exhibits medial energy density and power density. In this work, the high energy character of a lithium–air battery and the high power character of a supercapacitor were united together in one device. Thereby, the proposed lithium–air capacitor–battery based on a hybrid electrolyte has the potential to satisfy the various operating conditions of future EVs.

Experimental

The preparation of the Mn_3O_4 based air catalytic electrode is given in the previous report of Wang *et al.*[21] The area of the air catalytic electrode is 1 cm^2, and the mass loading of catalyst layer is 5 mg cm^{-2}. The capacitor electrode was prepared by mixing activated carbon (AC) powder (85%), polytetrafluoroethylene binder (PTFE) (10%) and acetylene black powder (5%). The area of the capacitor electrode is 2 cm^2, and the mass loading of the AC is 10 mg cm^{-2}.

The structure of the developed lithium–air capacitor–battery can be summarized as (see Fig. 1): I) a non-aqueous electrolyte (1 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate) and an aqueous electrolyte (4 ml 1 M KOH) are separated by a LISICON film. II) The Mn_3O_4 based air catalytic electrode is applied in an aqueous electrolyte. III) The prepared AC electrode serves as an additional capacitor electrode in the organic electrolyte solution. The water-stable lithium super-ionic conductor glass film (LISICON, $Li_{1+x+y}A_xTi_{2-x}Si_yP_{3-y}O_{12}$) with a thickness of 0.15 millimetres is provided by Ohara Inc., Japan. Its conductivity is 10^{-4} S cm^{-1}. Electrochemical tests were performed using a Solartron Instrument Model 1287 controlled by a computer.

References

1 A. Armand and J.-M. Tarascon, *Nature*, 2008, **451**, 652–657.
2 Y. G. Wang and H. S. Zhou, *Energy Environ. Sci.*, 2011, **4**, 1704–1707.
3 G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson and W. Wilcke, *J. Phys. Chem. Lett.*, 2010, **1**, 2193–2203.
4 K. M. Abraham and Z. Jiang, *J. Electrochem. Soc.*, 1996, **143**, 1–5.
5 T. Ogasawara, A. Débart, M. Holzapfel, P. Novák and P. G. Bruce, *J. Am. Chem. Soc.*, 2006, **128**, 1390–1933.
6 A. Débart, J. L. Bao, G. Armstrong and P. G. Bruce, *J. Power Sources*, 2007, **174**, 1177–1182.
7 A. Débart, A. J. Paterson, J. L. Bao and P. G. Bruce, *Angew. Chem., Int. Ed.*, 2008, **47**, 4521–4524.
8 W. Xu, J. Xiao, D. Wang, J. Zhang and J.-G. Zhang, *Electrochem. Solid-State Lett.*, 2010, **13**, A48–A51.
9 D. Zhang, Z. Fu, Z. Wei, T. Huang and A. S. Yu, *J. Electrochem. Soc.*, 2010, **157**, A362–A365.
10 X. H. Yang, P. He and Y. Y. Xia, *Electrochem. Commun.*, 2009, **11**, 1127–1130.
11 C. O. Laoire, S. Mukerjee and K. M. Abraham, *J. Phys. Chem. C*, 2010, **144**, 9178–9186.
12 http://www.almaden.ibm.com/institute/2009/.
13 Y.-C. Lu, Z. Xu, H. A. Gasteiger, S. Chen, K. Hamad-Schifferli and S.-H. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 12170–12171.
14 P. Kichambare, J. Kumar, S. Rodrigues and B. Kumar, *J. Power Sources*, 2011, **196**, 3310–3316.
15 C. Ó. Laoire, S. Mukerjee, E. J. Plichta, M. A. Hendrickson and K. M. Abraham, *J. Electrochem. Soc.*, 2011, **158**, A302–308.
16 X. Wu, V. V. Viswanathan, D. Y. Wang, S. A. Towne, J. Xiao, Z. Nie, D. H. Hu and J.-G. Zhang, *J. Power Sources*, 2011, **196**, 3894–3899.
17 A. C. Marschilok, S. Zhou, C. C. Milleville, S. H. Lee, E. S. Takeuchi and Kenneth J. Takeuchi, *J. Electrochem. Soc.*, 2011, **158**, A223–A226.
18 A. Kraytsberg and Y. Ein-Eli, *J. Power Sources*, 2011, **196**, 886–893.
19 B. Scrosati, J. Hassoun and Y.-K. Sun, *Energy Environ. Sci.*, 2011, **4**, 3287–3295.
20 Y.-C. Lu, D. G. Kwabi, K. P. C. Yao, J. R. Harding, J. Zhou, L. Zuin and S.-H. Yang, *Energy Environ. Sci.*, 2011, **4**, 2999–3007.
21 F. Mizuno, S. Nakanishi, Y. Kotanl, S. Yokoishi and H. Iba, *Electrochemistry*, 2010, 78403–405.
22 S. Visco and J. E. Nimon, LMLB 12th Meeting, Abs. 397.
23 Y. G. Wang and H. S. Zhou, *J. Power Sources*, 2010, **195**, 358–361.
24 Y. G. Wang and H. S. Zhou, *Chem. Commun.*, 2010, **46**, 6305–6307.
25 H. S. Zhou, Y. G. Wang, H. Q. Li and P. He, *ChemSusChem*, 2010, **3**, 1009–1019.
26 P. He, Y. G. Wang and H. S. Zhou, *Electrochem. Commun.*, 2010, **12**, 1686–1689.
27 P. He, Y. G. Wang and H. S. Zhou, *J. Power Sources*, 2011, **196**, 5611–5616.
28 E. J. Yoo and H. S. Zhou, *ACS Nano*, 2011, **5**, 3020–3026.
29 A. S. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Barde, P. Novak and P. G. Bruce, *J. Am. Chem. Soc.*, 2011, **133**, 8040–8047.