Imidazole-buffered acidic catholytes for hybrid Li-air batteries with high practical energy density

Longjun Li, Yongzhu Fu, and Arumugam Manthiram*

Materials Science and Engineering Program & Texas Materials Institute

The University of Texas at Austin

Austin, TX 78712, USA

Abstract

Hybrid Li-air batteries with acidic catholyte offer high cell voltage and are stable with CO₂ in air. However, the practical capacity of the acidic catholyte is limited by the low concentration of acids utilized and the limited solubility of the discharge products. Only weak acids or diluted strong acids with limited practical capacity are generally used due to the poor stability of the solid electrolyte in low pH solution. We show here the pH of high-concentration, strong acids can be increased to near neutral values by forming a buffer with imidazole additive, which can be used in hybrid Li-air batteries. With the addition of 6.06 mol L⁻¹ of imidazole to 6 mol L⁻¹ HCl, the solution has a mild pH of ~ 5.0, facilitating the operation of hybrid Li-air batteries with high practical capacity and stability.

Keywords: Hybrid Li-air cell; acidic catholyte; imidazole; catholyte; energy density

*Corresponding author. Tel: +1-512-471-1791; fax: +1-512-471-7681.

E-mail address: manth@austin.utexas.edu (A. Manthiram)

1. Introduction

Li-air batteries have attracted world-wide attention since the first aprotic Li-O₂ cell reported in 1996 [1]. Due to the high capacity of the lithium-metal anode and inexhaustible O₂ in air, aprotic Li-O₂ batteries offer high theoretical energy densities nearing that of gasoline [2]. However, with more recent calculations, the system-level energy density of aprotic Li-O₂ batteries is limited by accessories that are needed to keep the battery in a dry oxygen environment [3]. Hybrid Li-air batteries, in contrast, can be operated in ambient environment, holding promise to increase the system-level energy density [4-9].

Depending on the pH value of the catholyte in hybrid Li-air batteries, there are two kinds of reversible cathodic reactions. With an alkaline catholyte, the cell reaction is $4 \text{ Li} + \text{O}_2 + 2 \text{ H}_2\text{O} \leftrightarrow 4 \text{ LiOH}$. However, with the discharge process progresses, the concentration of LiOH increases gradually, leading to a soaring pH value of the catholyte, corroding the solid electrolyte, and depositing solid LiOH on the air electrode or solid electrolyte, and terminating the cell reaction [10, 11]. With an acidic catholyte, the cell voltage is higher based on the Nernst equation $E = E^\circ - 0.059 \times \text{pH}$. In addition, acidic catholyte does not uptake CO₂ from air, enabling the operation of the cell in ambient conditions. Earlier investigations mainly focused on weak acidic solutions, such as acetic acids and phosphate buffer [12, 13], due to the instability of the solid electrolyte in strong acids. However, acetic acid is volatile and lithium phosphate has low solubility in water, which limit the practical capacity of the

catholytes. Strong acids, such as sulfuric acid, were also explored. But only relatively low concentration can be used due to the corrosion of solid electrolytes in high-concentration strong acids [5, 6]. Inactive water takes up most of the weight in the catholyte, decreasing the practical energy density of the catholytes.

To solve this problem, we present here a novel approach to utilize high-concentration, strong acids (*e.g.*, 6 M HCl), while maintaining the pH of the catholyte near neutral. The key is to add an equivalent amount of imidazole to the acid solution. Imidazole is a modest base which can accept protons in water. After adding an equivalent amount of imidazole to a strongly acidic catholyte, protons are stored in the imidazole-acid complex, leading to a neutral pH of the catholyte.

2. Experimental

The morphology of the $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LTAP, 0.15 mm thick, $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, OHARA Inc., Japan) membrane was characterized by a scanning transmission electron microscope (STEM, Hitachi S5500) at an operating voltage of 30.0 kV and a current of 20 μA . The cyclic voltammetry (CV) plot of Pt/C in the imidazole buffer solution was recorded in a standard three-electrode glass cell with an electrochemical workstation (CH Instruments, Inc.) [14]. A glassy carbon electrode with a diameter of 3 mm was polished to a mirror-like finish before serving as the working electrode. The counter electrode was a Pt wire. A saturated calomel reference electrode (SCE) worked as the reference electrode. The catalyst ink was made by sonicating 5 mg of commercial 40 wt. % Pt on carbon

support (Johnson Matthey) and 15 μL of Nafion solution (5 wt. %) in a mixture of deionized water and ethanol (2 mL, 1:1 v/v). 2 μL of the catalyst ink was then loaded onto the glassy carbon electrode followed by drying in air. The electrolyte (1 M HCl + 1.01 M imidazole + 1 M LiCl) was bubbled with high purity nitrogen or oxygen gas for 30 min before each test. The CVs were recorded in the range of -0.7 to 1.1 V vs. SCE at a scan rate of 50 mV s^{-1} . The Li-air battery set-up and air-electrode preparation can be found in our previous publications [15]. The anode electrolyte consisted of 1 M LiPF_6 dissolved in ethylene carbonate/diethyl carbonate (EC/DEC) (1:1 v/v). 0.2 mL of 6 M HCl + 6.06 M imidazole + 1 M LiCl acted as the catholyte. All experiments were conducted at room temperature.

3. Results and discussion

As seen in Table 1, the practical capacity increases substantially with increasing concentration of acid in the catholyte. For example, with 6 M HCl in the catholyte, the capacity based on the whole catholyte is 136 mAh g^{-1} , which is more than 50 times higher than that of 0.1 M HCl. All catholytes contain 1 M LiCl to conduct Li^+ ions. The problem of increasing the concentration of acids is the corrosion of the LTAP electrolyte [16, 17]. The pH can be increased by adding a large amounts of supporting salts (*e.g.* CH_3COOLi in CH_3COOH [18], LiH_2PO_4 in H_3PO_4 [13]), but they decrease the practical energy density. Also, the supporting salts are usually the same as the discharge products, decreasing the capacity of the catholyte to accommodate discharge products. Moreover, this approach is not applicable to strong

acids (*e.g.*, HCl, H₂SO₄, and HClO₄) due to their low dissociation constants making the pH value low even with high concentration of supporting salts. In contrast, imidazole can be protonated on the nitrogen atoms, providing a means of storing protons and increasing the pH.

Fig. 1a shows the combining of imidazole and HCl to form an acid-base complex that has a dissociation constant of 7.0 [19]. Based on the dissociation constant, the pH values calculated for 1, 3, and 6 M HCl solutions as a function of imidazole concentration are plotted in Fig. 1b. As seen, HCl solutions with an equivalent amount of imidazole have a pH of 3.5, and to obtain a pH value of 5, a 1 % excess imidazole than HCl is needed in the catholyte. Accordingly, we prepared 1, 3, and 6 M catholytes by mixing pure imidazole powder and concentrated HCl solution (12.1 M) in a molar ratio of 1:1.01 and measured their pH to be around 5.0. To explore the stability of LTAP membranes in these catholytes, the LTAP membranes were then immersed in 0.1 M HCl or HCl + imidazole solutions of various concentrations and examined by SEM. Fig. 1c shows the SEM images of pristine LTAP with a porous feature, which is in agreement with previous reports [16, 17]. Fig. 1d shows the SEM images of LTAP after immersing in 0.1 M HCl for a month. The surface is completely changed after the immersion with the observation of nanoparticles underneath the surface. This is due to the fact that the polished top surface layer has been etched away in 0.1 M HCl solution. In contrast, the SEM image in Fig. 1e of the LTAP membrane after immersing for 2.5 months in a 0.1 M HCl +

1.01 M imidazole solution with a pH of ~ 5.0 reveals no observable change in the surface of LTAP. We also tested in solutions up to 6 M HCl + 6.06 M imidazole for 2.5 months and the LTAP membrane was still very stable as shown in Fig. 1f.

Although imidazole can stabilize the solid electrolyte in highly concentrated HCl, the solution has a low oxidation potential, as shown in Fig. 2a. A very sharp oxidation peak at ~ 1.1 V vs. SCE can be observed in 1.0 M HCl + 1.01 M imidazole with Pt/C catalyst loaded onto a glassy carbon electrode. In contrast, there is no apparent oxidation peak in the $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ buffer solution with the same pH value (5.0). The oxidation peak is not due to oxygen evolution reaction because no oxygen bubbles were observed during the oxidation process and no oxygen reduction reaction peak was detected when the potential was swept back. Instead, a dark brown decomposition product was found on the surface of the electrode, which could only come from imidazole oxidation. The oxygen reduction reaction (ORR) peak at ~ 0 V vs. SCE is much higher than the reduction peak of imidazole shown in Fig. 2b. In fact, imidazole has been used as an additive in the membrane of proton exchange membrane fuel cells [20-22], proving its stability during the ORR process. These results indicate imidazole-containing catholyte can be used in the discharge process, but not in charge process, of the hybrid Li-air batteries.

The discharge voltage profile of a hybrid Li-air cell with 6 M HCl + 6.06 M imidazole catholyte is shown in Fig. 2c. The current density is 0.5 mA cm^{-2} with a total of 0.2 mL catholyte in the cell. The cell was continuously discharged for ~ 110 h,

which leads to a specific capacity of 734 mAh g⁻¹ based on the 6 M HCl in the catholyte. The specific capacity based on the whole catholyte is 136 mAh g⁻¹. The catholyte can be easily recycled as shown in Fig. 2d. LiCl can be easily separated from the discharged solution by distillation due to the much higher boiling point of LiCl (2520 °C) compared to H₂O (100 °C) and imidazole (~ 90 °C). While the mixture of H₂O and imidazole can be directly applied again in the fresh catholyte, LiCl can be used for the production of lithium metal by electrolysis at 450 °C [23]. The byproduct Cl₂ can be turned into the active material (HCl) by reaction with H₂. The low-cost, high-energy, and recyclable features of the imidazole buffer make it appealing for application in large-scale hybrid Li-air batteries. The concept demonstrated here with imidazole buffer also inspires the exploration of more stable base molecules with high oxidation potentials, which can be applied in rechargeable hybrid Li-air batteries. In addition, there are a lot of developments recently on bifunctional catalysts for hybrid Li-air batteries [24-28]. It would be helpful to find a catalyst which possesses higher overpotential for imidazole oxidation to suppress the side reaction during the charge process.

4. Conclusions

In summary, we have successfully developed a new type of imidazole buffer catholyte with high practical energy density for hybrid Li-air batteries. The cell exhibits a high practical discharge capacity due to the utilization of small-molecule, high-concentration, strong acids. The cell exhibits very good stability due to the near

neutral pH value of the catholyte facilitated by imidazole. The imidazole buffer solution proves to be a promising catholyte for primary hybrid Li-air batteries, and exploration of other oxidatively stable bases could enable rechargeable hybrid lithium-air batteries.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DE-SC0005397.

References

- [1] K.M. Abraham, Z. Jiang, A polymer electrolyte-based rechargeable lithium/oxygen battery, *J. Electrochem. Soc.* 143 (1996) 1-5.
- [2] G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, W. Wilcke, Lithium-air battery: Promise and Challenges, *J. Phys. Chem. Lett.* 1 (2010) 2193-2203.
- [3] K.G. Gallagher, S. Goebel, T. Greszler, M. Mathias, W. Oelerich, D. Eroglu, V. Srinivasan, Quantifying the promise of lithium-air batteries for electric vehicles, *Energy Environ. Sci.* 7 (2014) 1555-1563.
- [4] S.J. Visco, Y.S. Nimon, B.D. Katz, US Patent 7,282,296 B2.
- [5] Y. Li, K. Huang, Y. Xing, A hybrid Li-air battery with buckypaper air cathode and sulfuric acid electrolyte, *Electrochim. Acta* 81 (2012) 20-24.
- [6] K. Huang, Y. Li, Y. Xing, Increasing round trip efficiency of hybrid Li-air battery with bifunctional catalysts, *Electrochim. Acta* 103 (2013) 44-49.
- [7] Y. Li, Z. Huang, K. Huang, D. Carnahan, Y. Xing, Hybrid Li-air battery cathodes with sparse carbon nanotube arrays directly grown on carbon fiber papers, *Energy Environ. Sci.* 6 (2013) 3339-3345.
- [8] L. Li, A. Manthiram, O- and N-doped carbon nanowebs as metal-free catalysts for hybrid Li-air batteries, *Adv. Energy Mater.* (2014) doi: 10.1002/aenm.201301795.
- [9] L. Li, S.-H. Chai, S. Dai, A. Manthiram, Advanced hybrid Li-air batteries with high-performance mesoporous nanocatalysts, *Energy Environ. Sci.* 7 (2014) 2630-2636.

- [10] P. Stevens, G. Toussaint, G. Caillon, P. Viaud, P. Vinatier, C. Cantau, O. Fichet, C. Sarrazin, M. Mallouki, Development of a lithium air rechargeable battery, ECS Trans. 28 (2010) 1-12.
- [11] Y. Wang, H. Zhou, A lithium-air battery with a potential to continuously reduce O₂ from air for delivering energy, J. Power Sources 195 (2010) 358-361.
- [12] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, A novel high energy density rechargeable lithium/air battery, Chem. Commun. 46 (2010) 1661-1663.
- [13] L. Li, X. Zhao, A. Manthiram, A dual-electrolyte rechargeable Li-air battery with phosphate buffer catholyte, Electrochem. Commun. 14 (2012) 78-81.
- [14] L. Li, A. Manthiram, Dual-electrolyte lithium-air batteries: influence of catalyst, temperature, and solid-electrolyte conductivity on the efficiency and power density, J. Mater. Chem. A 1 (2013) 5121-5127.
- [15] L. Li, X. Zhao, Y. Fu, A. Manthiram, Polyprotic acid catholyte for high capacity dual-electrolyte Li-air batteries, Phys. Chem. Chem. Phys. 14 (2012) 12737-12740.
- [16] T. Zhang, N. Imanishi, Y. Takeda, O. Yamamoto, Aqueous lithium/air rechargeable batteries, Chem. Lett. 40 (2011) 668-673.
- [17] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, Study on lithium/air secondary batteries-Stability of NASICON-type

- lithium ion conducting glass-ceramics with water, *J. Power Sources* 189 (2009) 371-377.
- [18] Y. Shimonishi, T. Zhang, P. Johnson, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, A study on lithium/air secondary batteries—Stability of NASICON-type glass ceramics in acid solutions, *J. Power Sources* 195 (2010) 6187-6191.
- [19] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 82nd ed., CRC Press/Taylor & Francis, Florida, 2001.
- [20] Y.-Z. Fu, A. Manthiram, Nafion-imidazole- H_3PO_4 composite membranes for proton exchange membrane fuel cells, *J. Electrochem. Soc.* 154 (2007) B8-B12.
- [21] C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, A.B. Bocarsly, Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells, *J. Power Sources* 103 (2001) 1-9.
- [22] K.D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, J. Maier, Imidazole and pyrazole-based proton conducting polymers and liquids, *Electrochim. Acta* 43 (1998) 1281-1288.
- [23] S.S. Chadwick, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verl, Weinheim, 2006.
- [24] W. Yang, J. Salim, S. Li, C. Sun, L. Chen, J.B. Goodenough, Y. Kim, Perovskite $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{CoO}_{3-\delta}$ loaded with copper nanoparticles as a bifunctional catalyst for lithium-air batteries, *J. Mater. Chem.* 22 (2012) 18902-18907.

- [25] W. Yang, J. Salim, C. Ma, Z. Ma, C. Sun, J. Li, L. Chen, Y. Kim, Flowerlike Co_3O_4 microspheres loaded with copper nanoparticle as an efficient bifunctional catalyst for lithium–air batteries, *Electrochem. Commun.* 28 (2013) 13-16.
- [26] J.-K. Kim, W. Yang, J. Salim, C. Ma, C. Sun, J. Li, Y. Kim, Li-water battery with oxygen dissolved in water as a cathode, *J. Electrochem. Soc.* 161 (2014) A285-A289.
- [27] C. Sun, F. Li, C. Ma, Y. Wang, Y. Ren, W. Yang, Z. Ma, J. Li, Y. Chen, Y. Kim, L. Chen, Graphene- Co_3O_4 nanocomposite as an efficient bifunctional catalyst for lithium-air batteries, *J. Mater. Chem. A* 2 (2014) 7188-7196.
- [28] L. Li, A. Manthiram, Decoupled bifunctional air electrodes for high-performance hybrid lithium-air batteries, *Nano Energy* (2014) doi: 10.1016/j.nanoen.2014.07.002.

Figure Captions

Figure 1. (a) Schematic representation of how imidazole stores protons to keep the catholytes near neutral pH. (b) Calculation of the pH values of HCl + imidazole buffer with different amounts of imidazole additives. SEM images of (c) pristine LTAP and (d) after immersing in 0.1 M HCl for 1 month, and (e) after immersing in 0.1 M HCl + 1.01 M imidazole for 2.5 months, and (f) after immersing in 6 M HCl + 6.06 M imidazole for 2.5 months.

Figure 2. (a) CV of Pt/C in N₂-purged 1 M HCl + 1.01 M imidazole and K₂HPO₄-KH₂PO₄ buffer with a pH value of 5.0, (b) CV of Pt/C in 1 M HCl + 1.01 M imidazole with saturated O₂ or N₂, (c) discharge curve of hybrid Li-air battery with 6 M HCl + 6.06 M imidazole at a current density of 0.5 mA cm⁻², and (d) the schematic representation of recycled imidazole buffer catholyte for hybrid Li-air batteries.

Table 1. Calculated capacity and energy density of catholytes based on imidazole buffered HCl solutions. All catholytes contains 1 M LiCl to conduct Li⁺ ions

	Concentration (mol/L)	Density (g/mL)	Capacity (mAh/g _{catholyte})	pH	Voltage (V)	Energy density (Wh/kg _{catholyte})
0.1 M HCl	0.1	1.03	2.6	1	4.21	10.9
0.1 M (HCl + imidazole)	0.1	1.03	2.6	3.5	4.06	10.6
1 M (HCl + imidazole)	1	1.06	25	3.5	4.06	102
3 M (HCl + imidazole)	3	1.11	72	3.5	4.06	292
6 M (HCl + imidazole)	6	1.18	136	3.5	4.06	552

Figure 1

Figure 2

Graphical abstract