

## State of charge and cycleability of lithium oxygen batteries under different operation conditions

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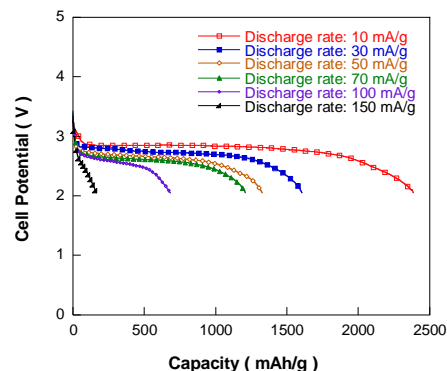
Li/air batteries are unique since lithium/oxygen couple provides the highest energy density among different materials yet investigated for advanced battery systems. The specific energy of lithium air batteries is an order of magnitude larger than that achievable using conventional lithium or lithium ion batteries [1]. At a nominal potential of about 3V, the free energy for the reaction of lithium with oxygen, forming  $\text{Li}_2\text{O}_2$  ( $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ ), is over  $11000 \text{ Wh kg}^{-1}$  [2] far exceeding Li-ion battery chemistry that has a theoretical specific energy of about  $400 \text{ Wh kg}^{-1}$ . Although the large free energy for the reaction of lithium with oxygen has attracted the interest of battery researchers for decades, as yet, commercialization of the Li/air cells has been mired by several problems such as their large capacity loss during cycling and their poor cycleability [3].

Since the purpose of a battery is to store energy and release it at the appropriate time in a controlled manner, apart from the basic battery design, its performance essentially depends on how and under which environmental conditions the battery is used. Operating conditions such as charge/discharge rate, charge/discharge temperature and charge/discharge depth govern the cycle life and load capability of the battery [4]. Li/air batteries are still in the early stage of their development, and their actual parameters fall far short of the theoretical values and even less is known about the effect of different operation conditions on their performance and there is nearly nothing published on the state of the charge conditions of these batteries.

In the present study several electrochemical parameters are investigated to optimize the state of the charge conditions of the Li/O<sub>2</sub> batteries. The results show the electrochemical performance and cycleability of the battery under different discharge rates, discharge depths and charge cut-off voltages which are very new and original research area for electrochemical energy storage.

The Galvanostatic discharge profiles at various discharge rates depicted in Figure 1 show that the effective capacity of the cell drops with increase in the discharge rate. The increased discharge current shortens the discharge plateau because of the increased polarization of cathode electrode. The discharge reaction at the cathode results in  $\text{Li}_2\text{O}_2$  being deposited within the pores of carbon electrode. At low discharge rates the deposit fills almost all pores in the electrode and discharge ends when there is no space available for further deposition of discharge products. As a result the electroactive surface area of the electrode is better utilized since pore filling occurs at slower rates. At high discharge rates the deposit only covers the electrode external surface and appears to be more of a film, which limits the discharge in the interior of the carbon by blocking its pores' entrance, rather than filling electrode's pores [5]. Although the capacity of the battery decreases however the cell's cycleability improves with increasing the rate of discharge probably due to the ease of stripping the  $\text{Li}_2\text{O}_2$  film formed on the electrode surface reversibly at higher

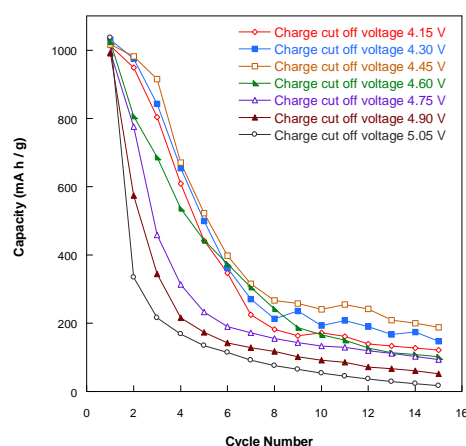
rates, compared with the incomplete removal of discharge products formed within the pores at lower rates.



**Figure 1:** Discharge profiles for Li/O<sub>2</sub> battery at rates between 10 and 150 mA g<sup>-1</sup>

The performance of the cell discharged at different cut off voltages showed that decreasing the depth of discharge decreases the rate of capacity fade and improves the cell cycleability. It was shown that controlling the discharge depth by restricting the discharge cut off voltage of the cell can be considered as a strategic method in balancing the specific capacity and cycleability of Li/O<sub>2</sub> batteries.

Study of the cell performance at different charge taper voltages (Figure 2) showed that both cell's capacity after the first discharge and its cycleability improve with increasing charge taper voltage for charge potentials up to 4.45 V. For charge potentials above 4.45 V, the cell performance deteriorates with increase in the charge taper voltage significantly, probably due to the decomposition of the electrolyte at higher charge potentials. It is believed that a potential of 4.45V is the edge of breakdown potential of propylene carbonate based electrolyte used in the battery.



**Figure 2:** Discharge capacity fade of Li/O<sub>2</sub> battery with cycling at different charge cut off voltages

## References

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