

Influence of CO₂ on the stability of discharge performance for Li-air battery with hybrid electrolyte based on the graphene sheet

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Recently, Li-air battery has attracted much more attention due to its extremely high specific energy density. However, there are still some critical problems such as air electrode's clogging and organic liquid electrolyte's decomposition during the discharge process. To overcome these problems, our group has developed a new type rechargeable Li-air battery based on a hybrid electrolyte with an aqueous electrolyte in the air electrode side [1,2]. However, there are also one major serious issue is the formation of Li₂CO₃ during electrochemical reaction, because the Li-air battery with alkali aqueous electrolyte has an open system and lead to react with Li⁺ ion and CO₂. The formation of Li₂CO₃ affects the diffusion rate and path for oxygen into air electrode to occur the reaction of chemical species with catalysts, and it is one of the reasons that discharge lifetime performance reduces due to block diffusion path of oxygen. Therefore, in order to improve the cell lifetime in Li-air battery with aqueous electrolyte, it is important to investigate the influence of CO₂ in air atmosphere for cell performance.

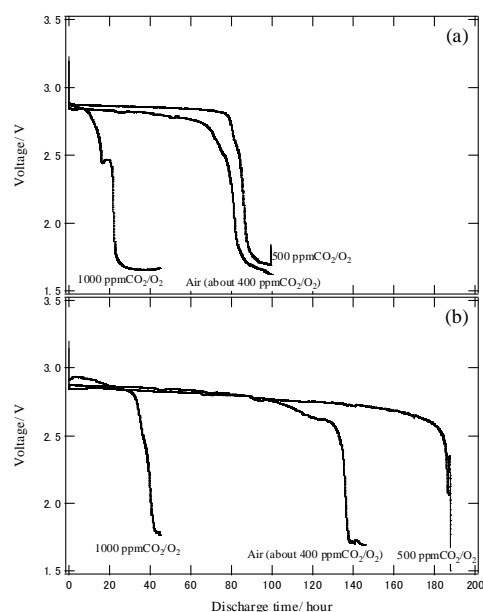


Figure 1 discharge performance of graphene nanosheet and commercial graphene sheet in the three different feed gases (a)commercial graphene sheet and (b) graphene nanosheet

In this study, we reported that the influence of CO₂ concentration on the cell lifetime of graphene sheet with different morphology, specific surface area and surface functional groups as used a cathode electrode in the Li-air battery with hybrid electrolyte. The graphene nanosheet was prepared by chemical method [3]. The commercial graphene sheet was purchased by ACS MATERIAL as a reference. The electrochemical test of both samples was measured in the 1M Li₂SO₄ + 0.5M H₂SO₄ as the aqueous electrolyte under three different atmospheres: air (about 400 ppmCO₂/O₂), 500 ppmCO₂/O₂ and 1000 ppmCO₂/O₂ to identify the effect of CO₂ on Li-air battery with hybrid electrolyte. A solid-state electrolyte Li_(1+x+y)Al_x(Ti,Ge)

{2-x}SiyP(3-y)O₁₂ (LISICON) film was used as a separating membrane between the organic and aqueous electrolytes to prevent intermixing of the two solutions. The cells were discharged at a current density of 0.5 mA/cm².

Figure 1 shows the discharge performance of graphene nanosheet and commercial graphene sheet as a function of the CO₂ concentration in the feed gas. Using air and oxygen containing 500 ppmCO₂ as feed gas, the cathode electrode was able to run about 70 and 80 h for commercial graphene sheet, respectively. Therefore, the lifetime of cathode electrode was kept for 20 h in the oxygen containing 1000 ppmCO₂. However, for the graphene nanosheet, the cathode electrode was able to run about for 140 and 180 h in the air and oxygen containing 500 ppmCO₂, respectively. Even in the oxygen containing 1000 ppmCO₂, the cathode electrode was able to run about 40 h. It is considered that this cathode potential loss for both samples is attributed to the Li₂CO₃ precipitation since insoluble Li₂CO₃ solid constituted physical barriers for mass transfer. This also indicated that the formation of Li₂CO₃ in the alkali electrolyte is strongly depending on the carbon materials.

Figure 2 shows the O1s XPS spectra before and after discharge process for both samples. The O 1s XPS spectra signify the formation of compounds such as Li₂CO₃ (531.6 eV) during discharge process for both samples as shown in the Figure 2. Additionally, the O1s spectra show clearly decreased intensity of functional groups after discharging, which provides the evidence of using functional groups as a nucleation of Li₂CO₃. It is thus considered that the functional group on surface of carbon is crucial factor to formation of Li₂CO₃. Furthermore, the specific surface area of carbon was measured by Brunauer-Emmett-Teller (BET) method. The specific surface area was estimated to be 820.5 and 204.3 m²g⁻¹ for commercial graphene sheet and graphene nanosheet respectively, indicating that the specific surface area is not influence the cell lifetime.

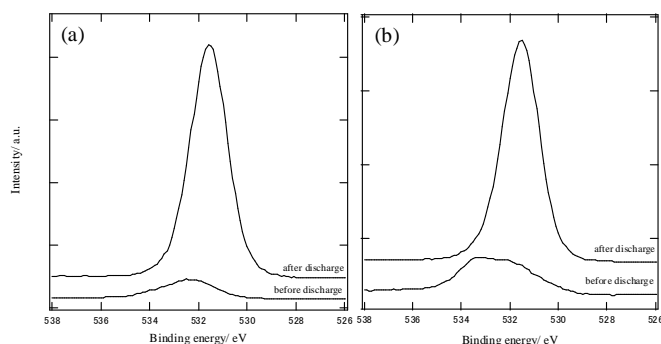


Figure 2 O1s XPS spectra of (a) graphene nanosheet and (b) commercial graphene sheet before and after discharging

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Acknowledgments

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