

A metal-free, Lithium-ion oxygen batteries for improving safety.

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Superbatteries having energy densities orders of magnitude higher than those of conventional electrochemical energy storage systems have been widely studied and discussed not only in the scientific literature[1] but also in popular books.[2] The most impressive example is the lithium-air battery, which in principle has an energy density of 11 420 Wh kg⁻¹. [3] In its most conventional configuration, the lithium-air battery is formed by a lithium metal anode; a separator embedded with a lithium-conducting, nonaqueous electrolyte; and a carbon (with or without catalyst) cathode. Oxygen gas is reduced at the cathode while lithium is oxidized at the anode, leading to the formation of lithium peroxide: $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$. This apparently simple process is, in reality, quite complex since it proceeds via a series of steps involving an intermediate $\text{O}_2^{\cdot-}$ radical anion species,[4] namely, a very strong base with high deprotonation activity that may seriously degrade the stability of the electrolyte. Indeed, as recently demonstrated, conventional lithium-ion electrolyte solutions, such as organic carbonates, cannot be used in lithium-air batteries because they decompose, leading to the rapid decay of the battery performance.

Even more problematic for the commercialization of the lithium-air battery is the use of lithium metal as the anode material. Lithium metal is in fact a very reacting electrode that may give rise to dendrite formation during cycling with associated serious safety hazards. Coverage of the lithium metal electrode by protective lithium-ion conducting films has been proposed to address this issue.[5] However, also this approach cannot ensure total safety, since the protective films are usually fragile and may easily deteriorate or even break upon battery operation.

In synthesis, there are three main issues that have so far prevented the full development of the lithium air battery; they are: (i) the instability of the electrolytes in the cell environment, (ii) the limited reversibility of the electrochemical process, and (iii) the reactivity of the lithium metal anode. The electrolyte issue has been addressed by searching media expected to be more stable than the common carbonate organic electrolytes, such as dimethoxy ethane-based solutions,[6] ionic-liquid-based solutions,[7] and poly(ethylene oxide)-lithium salt, for example, PEO-LiCF₃SO₃ polymer membranes,[8] however, with scarce success. Issue (ii) has been addressed by developing suitable cathode morphologies and also exploring the use of catalysts. The third issue has not even been considered since, to our knowledge, all of the Li-air works so far reported refer to batteries based on lithium metal as the anode.

In the present paper, we show that the issue may be successfully addressed by replacing the lithium metal anode by a lithiated silicon in combination with a stable

end-capped glyme electrolyte, such as to form a lithium-metal-free, lithium-ion, silicon-oxygen battery.

References

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