Researchers explore Li-air battery reversibility on the nanoscale

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(Phys.org) -- As their name suggests, Li-air batteries use air to operate, pulling out oxygen molecules to use in a porous, carbon-based cathode, while using lithium in the anode. Because using air means the battery doesn't have to store a heavy charge source at the cathode, the batteries can provide an extremely high energy density, holding nearly as much energy in a given volume as gasoline, and 5-10 times more than Li-ion batteries. Despite this major appeal, Li-air batteries still face many limitations that hold them back from commercialization. In a new study, a team of researchers has tackled one of these challenges: reversibility, which is necessary for being able to recharge the battery multiple times.

The researchers, Thomas Arruda, Amit Kumar, Sergei Kalinin, and Stephen Jesse at Oak Ridge National Laboratory in Tennessee, have published a paper in a recent issue of *Nanotechnology* in which they explore factors controlling the reversibility of the particle growth on an electrolyte underlying Li-air batteries and nanobatteries.

"We believe this work paves the way for studying irreversible or quasi-reversible nanoscale electrochemistry – in materials systems ranging from Li-air batteries to more established fields such as corrosion, electroplating, and many others," Kalinin told *Phys.org*.

"Primary Li batteries, which are non-rechargeable and disposable, have high energy densities and have been commercially available since the 1960s; however, they can only be used once," said Arruda. "In order for these cells to be competitive, for example, with fossil fuels (i.e., automotive applications), they need to be recharged hundreds, if not thousands, of times. Consider the average commuter refueling once per week. This equates to more than 500 fills over the course of a decade. An automotive Li-air battery would need to match this criterion, even without considering cost or other important metrics. In fact, reversibility remains the single most important and difficult task to achieve for Li-air batteries, as evidenced by the intense scrutiny of the leading battery experts."

When a charged Li-air battery is in use, the Li ions in the anode travel to the cathode, where they react with oxygen via an oxygen reduction reaction. The electrons resulting from this reaction are then harvested and used to provide electricity for electronic devices. To recharge the battery, the Li ions must travel from the cathode back to the anode. As the researchers explain, the reason it is so difficult to make Li-air batteries rechargeable is because the batteries combine the most difficult processes used in both batteries and fuel cells.

"Underpinning these processes is an abundance of unfavorable chemistries such as the poor solubility of reaction products (LiOx species), slow reaction kinetics, and the propensity of Li metal to react unfavorably with nearly everything," Jesse said. "For the case of the anode, the electrodeposition of Li ions to metallic Li often proceeds with the formation of needle-like Li particles called dendrites. These particles negatively affect the battery by (1) becoming disconnected from the anode and thus unavailable to participate in the reaction and (2) increasing the risk of an internal short circuit which could cause thermal runaway and fire. At the cathode, the oxygen reduction reaction remains as big a challenge for Li-air batteries as it is for fuel cells. When the two reactions are combined, they form a mixture of insoluble products which are difficult to react in reverse and eventually choke the cathode."

In their study, the researchers used an atomic force microscope (AFM) to investigate battery reversibility by analyzing the growth of Li particles. While sweeping the bias of a 20-nm AFM tip across the surface of a Li-ion conductive glass ceramic electrolyte, they measured the change in tip height during the cycling process. They found that increases and decreases in the tip height correspond to changes in current, allowing them to demonstrate the existence of reversibility as well as map the degree of reversibility at different locations.

In the future, the researchers hope to further improve the reversibility, and note that Li-air batteries still face many other challenges before they can become commercialized.

“Technological developments and systems engineering on all major components of Li-air batteries are required to bring this technology to market,” Kalinin said. “Better catalysts are needed on the cathode, Li anode protection without functional hindrance remains paramount, and superior multifunctional electrolytes need development. The ubiquitous necessity to understand fundamental processes at the most basic level of the key battery components remains a top priority. Only after a comprehensive understanding of the elementary processes is achieved can the chemistries be fine-tuned and the systems be properly engineered to meet the metrics demanded by the application.”

If researchers can overcome these challenges, Li-air batteries could potentially store energy for a wide variety of applications.

“If Li-air batteries could be realized, the primary application would be for transportation and other situations where mobility is necessary (like laptops, etc.) since they will be very lightweight for the amount of energy they store,” Arruda said. “Optimization of Li-air batteries to include a large number of charge/discharge cycles will drive down the cost and make fully electric vehicles a reality without the need for heavy batteries as is the current situation. Beyond this, it is easy to envision this technology (Li-air nanobatteries) being applied to microelectromechanical and nanoelectromechanical systems (MEMS and NEMS). These may be the ideal systems to employ such energy sources as they would have much lower energy demands and could operate for extended periods of time."

More information: Thomas M. Arruda, et al. "The partially reversible formation of Li-metal particles on a solid Li electrolyte: applications toward nanobatteries." *Nanotechnology* 23 (2012) 325402 (9pp). DOI: 10.1088/0957-4484/23/32/325402