Lithium-O\textsubscript{2} batteries hold promise for the next generation of electric vehicles and other applications. By reacting oxygen directly with lithium ions to form Li\textsubscript{2}O\textsubscript{2} on discharge, they can achieve energy densities 3-5 times higher than current lithium-ion batteries. Because Li\textsubscript{2}O\textsubscript{2} forms an electrically insulating film during discharge that passivates the electrode surface, obtaining optimal volumetric capacities requires an understanding of the mechanisms that control Li\textsubscript{2}O\textsubscript{2} film formation.

High volumetric capacities can be achieved by promoting the growth of large toroidal deposits of Li\textsubscript{2}O\textsubscript{2} as opposed to thin-films, which cut off cell discharge prior to full void space filling of the electrode. Li\textsubscript{2}O\textsubscript{2} can form by a surface pathway involving two-electron transfers into a film or by a solution pathway involving a one-electron transfer to create solvated LiO\textsubscript{2} that chemically forms toroidal Li\textsubscript{2}O\textsubscript{2}. We study the mechanisms of nucleation and growth by the surface pathway to promote more efficient void filling. Potentiostatic discharges provide useful information about the kinetics of the film formation as the driving force for Li\textsubscript{2}O\textsubscript{2} is fixed, which allows the application of existing models for electrodeposition to our system to extract rates of surface nucleation and growth. Our initial efforts have focused on performing potentiostatic discharges on carbon paper in a standard cell. This method shows that potential determines the rate of film growth (Figure 1), but it provides no means to separately characterize the mechanisms of the surface and solvent processes.

To distinguish current that forms Li\textsubscript{2}O\textsubscript{2} in solution from current that forms Li\textsubscript{2}O\textsubscript{2} on the electrode, we use the rotating ring disk electrode technique (RRDE). RRDE reduces oxygen at an inner disk electrode to form insoluble Li\textsubscript{2}O\textsubscript{2} on that electrode or soluble LiO\textsubscript{2} that is swept to an outer ring electrode by a convection current created by rotating the setup (Figure 2). Since we directly measure the amount of soluble species at the ring, we can calculate the amount of Li\textsubscript{2}O\textsubscript{2} formed by the surface pathway. This allows us to model the nucleation and growth kinetics of the surface film formation. We use RDDE to study how solvent properties and potential govern surface film growth kinetics, which will be key in achieving high void-filling high volumetric capacity Li-O\textsubscript{2} batteries.

FURTHER READING