PORE-SCALE TRANSPORT RESOLVED MODEL FOR LI-AIR BATTERIES

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ABSTRACT

Li-air battery, with its usable energy density close to 1,700Wh/kg, has captured worldwide attention as a promising battery solution for electric vehicles. However, current Li-air technology suffers from low round-trip efficiency and rate capacity. The electrode microstructure plays an integral role in the performance of the non-aqueous Li-air battery. In this work, a pore-scale transport resolved model of the non-aqueous Li-air battery has been developed that is capable of simulating the species/charge transport and reaction kinetics at the distinct phases of liquid electrolyte, solid electrode, and lithium peroxide. This pore-scale approach is in contrast to the more common volume-averaged model, which considers the domain as a homogenous medium of uniform porosity. Utilizing a pore-scale approach requires no simplification or assumptions regarding the electrode morphology, and has enabled the detailed studies into the effects of the precise electrode microstructure. A model for the thickness-dependent Li_2O_2 conductivity is developed based on inputs from the density functional theory (DFT) calculations and is incorporated into the pore-scale model to simulate the galvanostatic discharge of a nanostructured Li-air cell and validated by experiments. Good agreement is reached between the model and experiment, including the sudden drop in cell voltage at the end of discharge, which can not be recovered with the use of a constant Li_2O_2 conductivity. A critical insulation thickness of 12.6nm for the Li_2O_2 buildup on the electrode surface is identified, above which the electrode becomes insulating.

The validated model is then used to examine the effects of the applied current density, the ORR rate coefficient, and the electrode geometry on cell performance. The results indicate that both the discharge voltage and capacity decrease with applied current density. The cell discharge capacity is limited by the spacing between nanostructures, which may lead to pore blocking and hence the reduction of active surface area. For the system considered, an increase in nanostructure spacing from 4nm to 36nm leads to a 35% increase in the specific discharge capacity. The height of nanostructures can also influence the specific discharge capacity, and both the discharge voltage and capacity increase with the nanostructure height as a result of increasing active area. By increasing the nanostructure height from 4nm to 50nm, the specific discharge capacity increases by approximately 120%.

The pore-scale model greatly benefits from the kinetic-limited Li_2O_2 growth mechanism, although the real growth mechanism may also depend upon the choice of electrolyte, discharge current, and catalyst. The future work will extend the pore-scale model to three dimensions and examine the microstructural effects of digitally reconstructed electrodes, as well as the rate-dependent Li_2O_2 growth morphologies. The methodology presented here can be applied to any electrochemical system that includes an insoluble product formation as a result of the reaction process.