

Impedance Behavior of Binderless Ni-Mo Composite Cathode for a Li-O₂ Battery via Impedance Spectroscopy

R. Nelson, M. H. Weatherspoon, J. Kosivi, E. E. Kalu, J. P. Zheng

FAMU-FSU College of Engineering,
2525 Pottsdamer St, Tallahassee, FL, 32310

Lithium oxygen (Li-O₂) batteries have significant promise for energy storage, with a high theoretical energy density above 10 kW/kg (1). However, there are many shortcomings from a cyclability and efficiency perspective, leaving room for improvement. It is understood that most of the significant electrochemical activity is on the cathode side; hence, there is much work in cathode design improvement (2). Specifically, cathodes with metal oxide deposits have provided an improvement capacity and efficiency, leading to improved performance over cells with bare carbon cathodes (3).

We present a porous carbon cathode with an electroless deposited nickel and molybdenum (Ni-Mo) composite that was also electrolytically oxidized for use in Li-O₂ batteries. Cyclical charging and discharging, followed with impedance spectroscopy measurements, is performed to gather frequency dependent impedance behavior. Throughout cell cycling, there is greater polarization from product buildup (2). This increases the impedances of the cell and leads to a decrease in capacity. Unique to this study, we include the impedance response of the cell to high frequency voltage signals at 10 kHz and greater, where capacitive behavior is recessive. Typically, studies analyzing gas diffusion type cells attribute behavior at these frequencies to be inductive behavior from instrumentation, cathode design, or other factors (4). Results are presented that provide insight on the inductive behavior versus frequency and decreasing capacitance versus cycling of the cell as it relates to physical properties of the fabricated porous cathode.

Figure 1 illustrates the cell's increased impedance after cycling due to lithium product buildup on the cathode surface. Pore blockage, reduced surface area for oxygen reduction reactions, and electrolyte consumption are a few contributions to overall impedance growth. As frequency increases from 10 kHz, cell reactance becomes more negative which corresponds to a

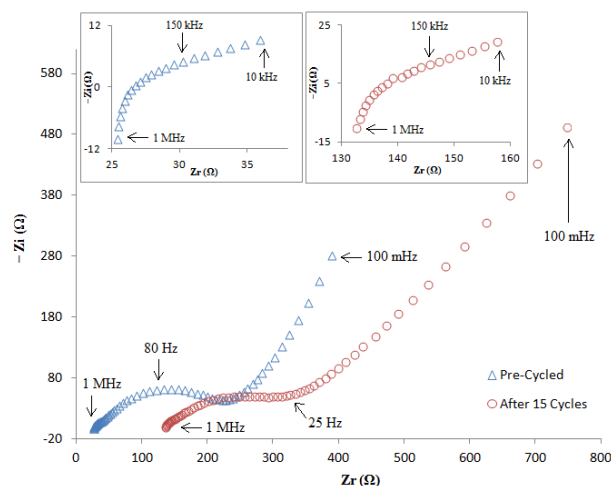


Figure 1: Impedance spectrum (1 MHz to 0.1 Hz) of cell with Ni-Mo composite oxide catalyst pre/post cycling.

decrease in cell capacitance. This capacitance is associated with the surface films on the cathode due to cycling. Figure 2 contains data that shows varying imaginary impedance versus frequency and discharging. A linear approximation of these impedance changes can represent the reactance growth rate over cycling and frequency as given in Figure 3. The slopes of these approximations get smaller as frequency increases, and this indicates a reduced rate of reactance change. Analyses starting at frequencies near 316 kHz reveal positive reactance values which indicate a net inductive behavior of the cell. Specifically at 1 MHz, the slope, or the rate of reactance impedance growth, is approximately zero and suggests that an overall inductive cell behavior can be maintained throughout cycling. Cell evaluation at high frequencies captures the effects of lithium oxide, carbonate, or other surface layer buildup on the cathode.

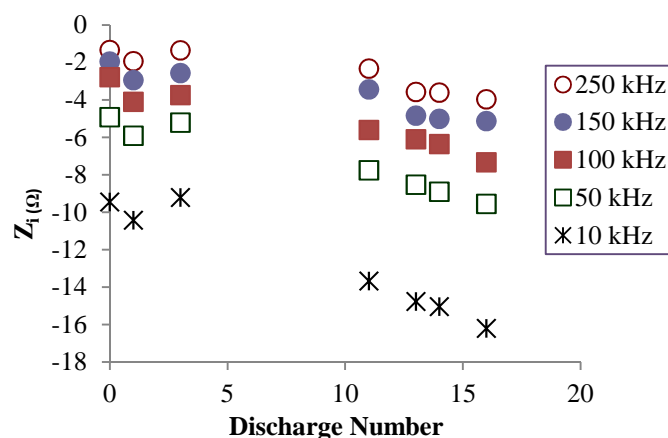


Figure 2: Cell reactance versus discharge and frequency.

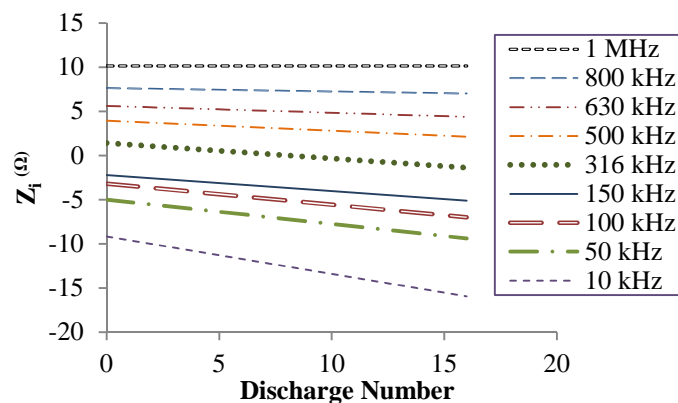


Figure 3: Linear approximation of cell reactance versus discharge and frequency.

Acknowledgement

This work was supported by the ERC program of the National Science Foundation under award number EEC-08212121.

References

1. J.P. Zheng, R.Y. Liang, M. Hendrickson, E.J. Plichta, *J. Electrochem. Soc.*, **155**, A432 (2008).
2. G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.*, **1**, 2193 (2010).
3. Y. Shao, S. Park, J. Xiao, J.G. Zhang, Y. Wang, J. Liu, *ACS Catal.*, **2**, 844 (2012).
4. M. Ciureanu, R. Roberge, *J. Phys. Chem. B*, **105**, 3531 (2001).