Ultra-High-Rate Pseudocapacitive Charge Storage in 3D Nanoporous Metal Scaffold-Supported Silver Oxide and Kinetics Analysis

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Abstract

Pseudocapacitors stand apart from batteries for their unique capability to quickly store and release energy by taking advantage of rapid oxidation and reduction (i.e. Faradaic) reactions at material interfaces. The Detsi Group demonstrated a pseudocapacitive charge storage approach where the working ion is part of the material. In their system, Ag^+ acts as the working ion in a non-aqueous electrolyte, where silver (I) oxide grown on a three-dimensional nanoporous gold (NP-Au) scaffold acts as the storage medium. Charge storage in the coin cell occurs through electron transfer involving oxidation and reduction reactions. In a non-aqueous electrolyte, Ag^+ acts as the working ion and Ag_2O acts as the storage medium. Through oxidation and reduction reactions of Ag_2O and Ag_2O_3, pseudocapacitive charge storage starts to occur.

Introduction

- A coin cell with stored pseudocapacitive charge from the oxidation and reduction reactions of Ag_2O and Ag_2O_3 is being used to graph a cyclic voltammogram (CV) curve.
- At different voltage positions of the CV curve, current is going to be different. As the scanning rate for the CV curve increases, the current increases as well.
- There are two different types of current: capacitive current (I_c) and Faradaic current (I_f). Hence, the total current can be expressed as a function of two different types of currents: I = Ic+If.
- Capacitive current is also known as "fast kinetics." During the reaction, charge transfer occurs at the electrode surfaces, not inside the electrode. Thus, there's no diffusion of ions inside the electrode.
- Faradaic current is also known as "slow kinetics." During the reaction, charge transfer occurs inside of the electrode. Thus, the whole process of the charge transfer is diffusion-limited.
- Kinetics analysis is being used to measure the capacitive current and Faradaic current through the equation: $I(V,v) = k_1V + k_2V^{1/2}$.
- Capacitive current is expressed through the equation $I_c = k_1V$ and Faradaic current is expressed through the equation $I_f = k_2V^{1/2}$.
- The goal was to find the capacitive current and compare it to the overall current in order to find the percent capacitive of the coin cell.

Methods and Materials

- Created a coin cell using nanoporous gold, glass fiber separator, crumpled silver, metal spacer, spring, and $AgNO_3$ & ACN electrolyte.
- Performed graphical analysis by creating a cyclic voltammogram (CV) curve at different scanning rates. The scanning rates vary from 1 mV/s to 1000 mV/s.
- To find percent capacitive of the coin cell, all of the curves' peaks had to be aligned at the smallest scanning rate.
- The equation $I(V,v) = k_1V + k_2V^{1/2}$ can be written down as $I(V,v)/V^{1/2} = k_1{*}\,V^{1/2} + k_2$ which is also a linear equation.
- After aligning the peaks, current values at every voltage position was used in order to create a table and a linear graph of «Current vs Voltage».
- By using the linear graph of «Current vs Voltage», it is possible to find the slope of the curve which will equal to the value of k_1.
- After finding k_1, it is possible to find the value of capacitive current by using the equation $I_c = k_1{*}V$.
- It is possible to find the percent capacitive through integrating capacitive current and overall current, and dividing them.

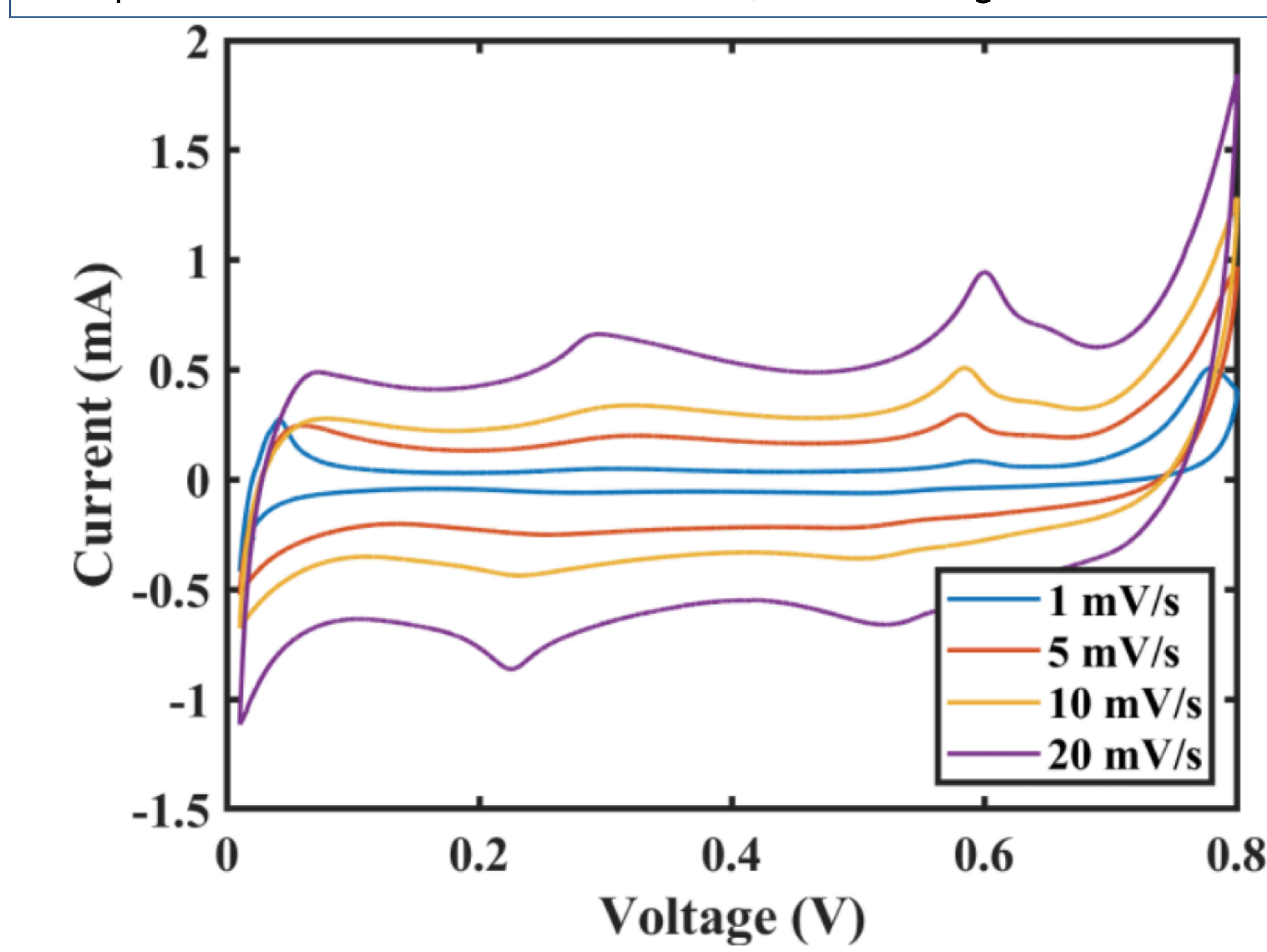

Chart 1. CV curve for scanning rates 1 - 20 mV/s

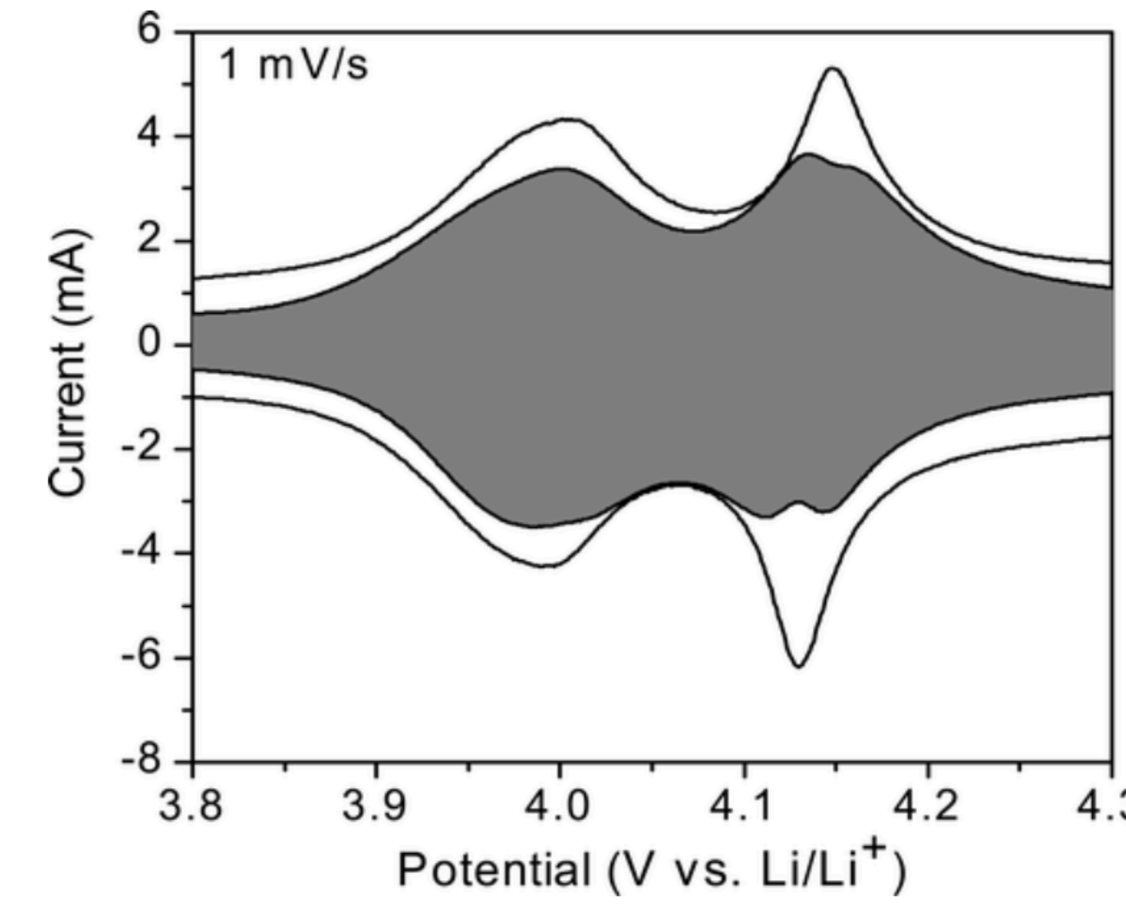

Chart 2. Expected contribution of capacitive current. Figure reproduced from Ref [1]

Results

- Three different CV curves have been obtained. The scanning rate for the CV curves have ranged from 1 to 50 mV/s, 100 to 400 mV/s, and 500 to 1000 mV/s. Chart 1 represents the CV curve with the scanning rate 1 to 20 mV/s.
- Rapid oxidation and reduction reactions occurred in the coin cell and charge was stored which can be seen in Chart 1.
- After performing Kinetics Analysis, first results were incorrect due to errors in shifting the peaks of the CV curve.
- MATLAB code for the Kinetics Analysis still has some issues and does not fully represent correct values. There are errors that have to be fixed.

Future Directions

- Fix all of the issues with the code in MATLAB.
- Compare my results with one of the graduate students who has performed Kinetics Analysis on the same data as me.
- After creating new coin cells in the lab and graphing their CV curves, use Kinetics Analysis code in order to find out percent capacitive of the created coin cell. (Expected result is shown in Chart 2 [1])
- Use Python coding platform in order to write the same code and compare the results.

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Works Cited

[1] Lesel, Benjamin K et al. "Mesoporous Li x Mn 2 O 4 Thin Film Cathodes for Lithium-Ion Pseudocapacitors." *ACS nano.* 10.8 (2016): 7572–7581.

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