EVALUATION OF THE STATE OF CHARGE OF BATTERY ELECTRODES WITH AC IMPEDANCE TECHNIQUES

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Part I

a. Papers Submitted to Refereed Journals (and not yet published):


b. Papers Published in Refereed Journals:


h. Invited Presentations at Topical or Scientific/Technical Society Conferences:

Recent invited talks on the subjects which are being sponsored by ONR were presented in the following locations:

1. Contributed Presentations at Topical or Scientific/Technical Society Conferences:


k. Number of Graduate Students Receiving Full Or Partial Support on ONR Contract: 2

1. Number of Postdoctoral Fellows Receiving Full Or Partial Support on ONR Contract: 0
Part II

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d. Project Description:

The main objective of this project was to study the correlations between the state of charge (SOC) of battery electrodes and the frequency dispersion of their impedance. Zinc and silver electrodes were investigated in smooth and porous configurations, under conditions similar to conventional battery applications. The emphasis was on the evolution of random morphologies of a composite dielectric as a function of the SOC and the ability of impedance measurements to quantify these changes. We seek theoretical and experimental tools that will help quantify the random morphologies and correlate them with the interfacial chemistry and wish to determine whether phase transitions in transport properties take place during the charge/discharge cycles and how best they can be categorized to provide predictive power for the transport properties in these systems.

e. Significant results during the last year:

* Image Processing: We have used the image processing setup, that was described in the previous report, to analyze the morphologies of zinc and silver over a broad potential range. The range of morphologies cover smooth deposits, morphologies which are dominated by nucleation through ones which are determined by diffusion limited aggregation that results in dendritic growth. The depositions were made both under galvanostatic and potentiostatic conditions and in various electrolytes. The chronopotentiometric and the chronoamperometric behavior was monitored parallel to the pattern evolutions.

The most significant results out of these efforts are summarized below:

1. Zinc Electrode: We have made significant progress on the study of the evolution of the pattern formations during electrodeposition of zinc. The images of zinc electrodeposition, in the two dimensional electrochemical cell that was described in the previous report, were digitized and analyzed for self similarity in terms of various fractal dimensions (surface, mass, etc.) in ways which makes possible comparison with the computer simulated patterns. The time evolution of each of these parameters was examined to determine which one can be associated with the process itself (time invariance). The process parameters were examined as to their dependence on macroscopic electrochemical parameters such as overpotential, concentration, electrolytes, etc. The kinetic parameters of the electrodeposition in the two dimensional cell were found to be in agreement with those derived in the three dimensional cell under similar conditions. The main conclusion out of these efforts was that for systems without supporting electrolytes, the potential regime in which the DLA pattern emerges agrees with the potential of the onset of the diffusion limiting current thus lending some credence to the simplified assumptions
often used in the computer simulations. The current-time behavior at various potentials was monitored and the results were analyzed in terms of Abyaneh - Fleischmann theories of electrochemical nucleation. The same experiments were tried with a variety of supporting electrolytes with resulting pattern formation that is not in agreement with the computer simulations. A complicating factor under these conditions is the competing hydrogen evolution reaction which is not a factor in the absence of the supporting electrolytes and was never included in any of the computer simulation models.

2. Silver Electrode: The methodology follows closely the one that was described for the zinc electrode, albeit with considerably less details. Since the emphasis here was on the impedance measurements, description of which will follow, the emphasis was on the controlled oxidation of these patterns. The deposition here was done from AgNO_3 solutions and once the deposits with the desired morphology formed, the electrolyte was carefully washed out and replaced by KOH in which the oxidation took place. The morphologies were analyzed and the setup was transferred for impedance measurements.

* Impedance: The impedance of the oxidized and metallic silver deposits were analyzed over the frequency range of 1 mHz - 10 MHz, using the impedance setup that was described in the previous report. The equivalent circuit was established and the origin of the elements investigated through their dependence on such parameters as concentration of the electrolyte and total charge that was required for deposition of the two oxides. In all cases a CPA (Constant Phase Angle) element was required. The exponent of the CPA element was compared with the fractal dimension. The results were analyzed in terms of two theoretical models: a. \( n = 1/d_f \) - the reciprocal model (Le-Mehaute and Nyikos&Pajkossy) and b. \( n = 2 \) - the linear model (Liu); where \( n \) is exponent of the CPA element and \( d_f \) is the two dimensional surface fractal dimension (contour of the two dimensional surface). The results favor the reciprocal model, however the most surprising conclusion is that the correlation is independent of the dielectric properties of the interface since the data for the oxidized and unoxidized silver fall on the same correlation curve. This conclusion negate most of the theoretical approaches to this problem since they were all based on scaling of a rectifying interface.

* Organic Polymers: The work on the random network modeling of a random distribution of conducting fibers in an electrolyte was finished in this reporting period. We have used Monte-Carlo calculations to calculate the intrachain and intrafiber contributions to the conductivity and compare the results with experiment. The two main points of interest that have emerged out of this work are:

1. For lightly dopped polymers the resistivity of the film is related to the resistivity of individual fibers through the following relationship:

\[
\sigma_{\text{fm}} = \sigma_{\text{fr}} \left(\frac{1}{p}\right)^2 v
\]

where \( \sigma_{\text{fm}} \) is the conductivity of the film, \( \sigma_{\text{fr}} \) is the conductivity of an average fiber, \( l \) is the thickness of the film, \( p \) is the average path length of the signal across the film and \( v \) is the volume fraction of the film. Since the geometrical factors can be correlated with the morphology
of the film this equation can serve to correlate the morphology with the conductivity of the film.

2. For films with higher conductivity one can always find a frequency regime where CPA behavior dominates the impedance. The CPA exponent was found to change with the morphology of the film. We have also found that the number of intersections between fibers is self similar due to the random distribution of small and large fibers. We have found that the exponent of the CPA, \( n \), relates to the fractal dimension, \( D \), of the number of intersection points through:

\[
    n = D - 1
\]

f. **Plans for next year's work:** This is the last report of the current program.
g. **Personnel:**

1. Mr. Galathara L. Kahandra - Graduate student
2. Mrs. Chandralekha Barve - Graduate student

h. **Technical Reports:**

25. Fractality and Impedance of Electrochemically Grown Silver Deposits.