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Quantitative Nano-scale AFM Impedance Imaging: Application to ORR Kinetics

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Recently, several research groups have developed impedance microscopy systems that allow highly localized AC measurements to be acquired at the sub-micron length scale[1-3] So far these systems have been used mainly in *qualitative* imaging modes to produce 2D maps or images of impedance variations across sample surfaces. The technique has been successfully applied to visualize electronic conductors, electro-ceramics, and ionic conductors with sub-micron resolution. (See, for example, Fig. 1.) Nanometer scale visualization and measurement of impedance promises to be a valuable tool for a wide variety of fields, including solid state ionics, semiconductors, coatings and corrosion research, and battery and fuel cell systems. Unfortunately, the technique is currently limited by an inability to acquire *quantitative* impedance information.

More generally, many other local-probe techniques currently suffer from the same limitation. Extracting quantitative information from scanning spreading resistance microscopy[4], conductive AFM[5], tunneling-AFM[6], and scanning capacitance microscopy[7] has also proved difficult.

Here, we present a methodology for the extraction of quantitative data from AFM impedance measurements. While this work focuses specifically on application to the AFM impedance technique, it may be easily extended to a variety of other local-probe measurements. The methodology depends critically on the ability to quantitatively characterize the AFM-tip/sample contact. Concepts and results from the fields of nanoindentation and contact mechanics provide this critical link. Using results from nanoindentation experiments, tip/sample contact forces measured in the AFM can be converted into tip/sample contact area estimates. A model for the tip/sample contact is then proposed which allows quantitative assignment of the impedance results based on the contact area estimates.

The methodology is validated by AFM impedance studies of the oxygen reduction reaction (ORR) at nanoscale Platinum/Nafion contacts. The quantitative kinetic data obtained from the AFM impedance technique is shown to match well with previous bulk measurements. Furthermore, measurements acquired over a wide range of tip/sample forces show good linearity with little scatter, as shown in Fig. 2. After correcting for the estimated tip/sample contact areas, a range of AFM impedance measurements acquired at different forces all produce approximately the same kinetic result with a small standard deviation--- illustrating the technique's capability to achieve reliable quantitative results.

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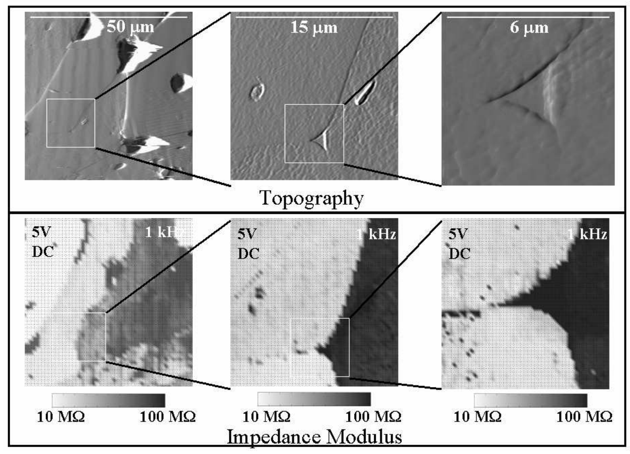

Figure 1: AFM topography deflection (top row) and impedance modulus (bottom row) images, increasing in magnification from left to right from a ZnO varistor sample. (50□m, 15□m, and 6□m scan regions, respectively.) Impedance-modulus images were acquired at 1 kHz with a 100 mV excitation signal and 5V DC bias. The images “zoom” into a triple-junction region between 3 ZnO grains. The V-like intrusion between the 3 grains is a highly insulating Bi_2O_3 second phase inclusion. (Confirmed by EDX analysis.)

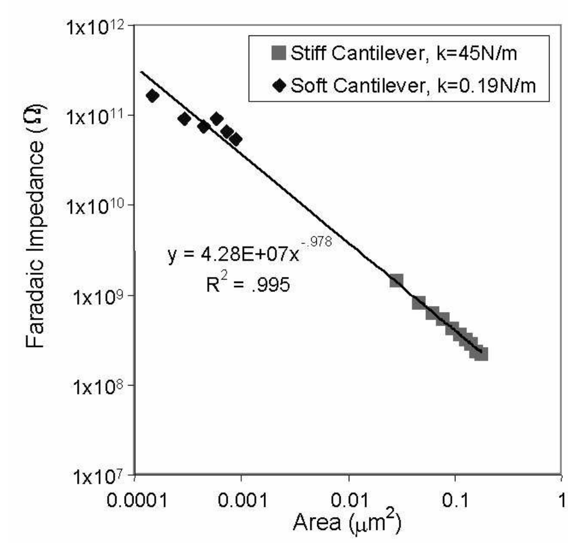

Figure 2: Faradaic impedance measurements of the oxygen reduction reaction at nanoscale Platinum/Nafion contacts acquired using the AFM impedance system. The data, acquired over a range of contact forces (corrected to contact area estimates) shows good linearity with little scatter. As indicated by the power law fit, the Faradaic impedance scales with the inverse of the contact area. (■)Data acquired using stiff cantilever geometry (k = 45N/m) (♦)Data acquired using soft cantilever geometry (k = 0.19N/m)