THE EFFECT OF ELECTROCHEMICAL POTENTIAL ON CONDUCTANCE OF Au NANOCONTACTS

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Conductance quantization of metal nanocontacts mechanically formed at RT has been studied recently in several electrochemical environments [1-5]. In these experiments, different reactions (i.e. adsorption or desorption of molecules or ions) at the metal surface can take place that can be controlled by the electrochemical potential of the nanocontact relative to a reference electrode in the electrolyte. At positive potentials, well defined peaks at integer multiples of G_0 ($2e^2/h$) are observed in the conductance histograms of Au (much like in air or vacuum), while under the hydrogen evolution reaction (negative potentials), a well defined fractional conductance peak appears near $0.5G_0$. In order to explain this fractional conductance several mechanisms (i.e. hydrogen incorporated wire, dimerized wire) have been proposed. However, the actual origin is not clear at present.

In this work we present conductance measurements on Au nanocontacts formed at room temperature in several solutions and under electrochemical potential control. Fig.1 shows the cyclic voltammogram of Au in the 0.1 M HNO_3 solution. The hydrogen evolution proceeds at potentials lower than ~ -0.3 V, while the double layer regime proceeds between ~ -0.3 V and 0.8V. Fig.2 shows the histograms of Au in this electrolyte at different electrochemical potentials. At 0.25V (double layer regime, Fig. 2c) the histogram shows peaks near integer values of G_0, but when the potential decreases (hydrogen evolution, Fig.2b and 2a), the width of these peaks and the background in the histograms increase and peaks appear at fractional values of G_0 (the most important at $0.3G_0$). At $0.5G_0$ a shoulder is observed in the histogram at -0.5V (Fig.2a) in contrast with the intense peak reported in previous works [1-5]. Similar results are found using different electrolytes. At negative electrochemical potentials is expected that cations, such as H^+ (H_3O^+) accumulate at the nanocontact, and they may act as impurities or disorder centers. This behavior could explain the increase in the width and background in the histograms with the negative potential in agreement with theoretical works [6].

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Figures:

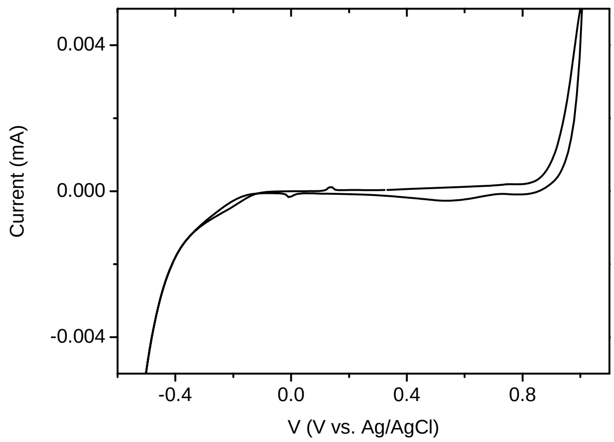

Fig.1. Cyclic voltammogram of Au electrode in 0.1 M HNO_3.

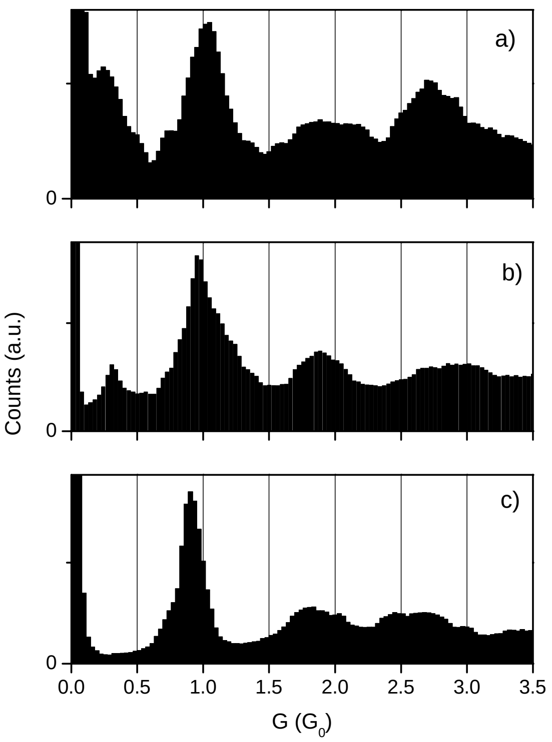

Fig2. Conductance quantization histograms of Au nanocontacts in 0.1 M HNO3 solution. The electrochemical potentials are: a) -0.5V, b) -0.3V and c) 0.25V.