ELECTROCHEMICAL POTENTIAL AND ELECTROLYTE EFFECT ON THE 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 has been reported 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.

Gold nanocontact conductance histograms are reported in this work as a function of the electrochemical potential in both pH neutral (salts) and acidic electrolytes. In contrast to the effect of a salt electrolyte, where the histogram peaks at integer values of G_0 become sharper at negative electrochemical potentials and few plateaus of fractional conductance are observed (Fig.1), acid solutions exhibit an apparent broadening of the peaks, which is actually due to the appearance of extra peaks at non-integer values of the quantum of conductance. These are due to the formation of extra stable structures due to the adsorption of atomic hydrogen and H_2 at the gold nanocontact [6].

At positive electrochemical potentials, near and in the beginning of oxygen evolution, the peaks at integer values of G_0 become skew at the left part of integer quantum conductance values, which is a symptom of an increase disorder due to the incorporation of oxygen atoms in the nanocontact. No fractional conductance values are observed in this region.. This behavior could explain the increase in the width and background in the histograms with the negative potential in agreement with theoretical works [7].

References:

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Figure:

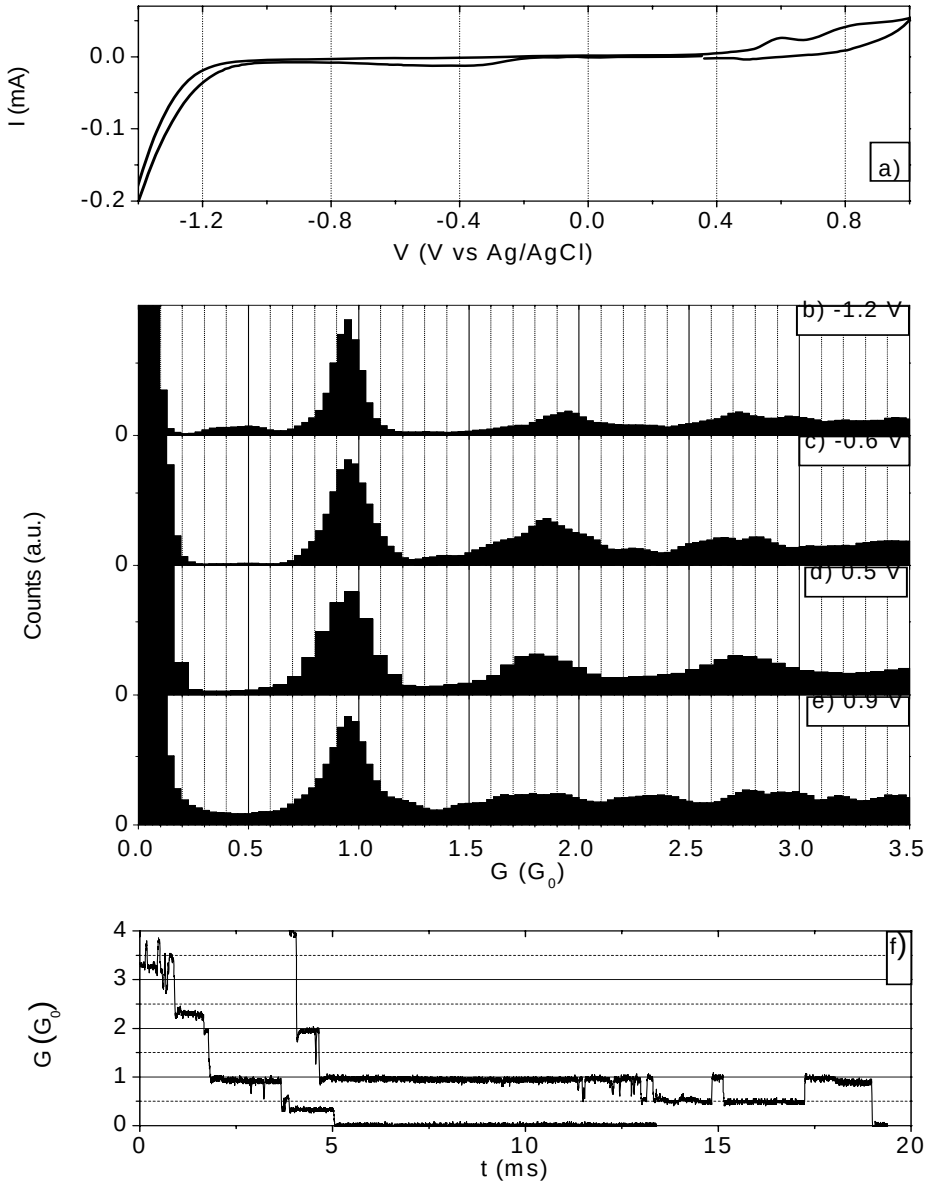

Fig.1. a) Cyclic voltammogram of the Au electrode in 0.1M $NaClO_4$. Conductance histograms of Au in this electrolyte at electrochemical potential: b) -1.2V, c) -0.6V, d) 0.5V, e) 0.9V and f) conductance traces of the Au nanocontacts in 0.1M $NaClO_4$ at electrochemical potential of -1.2V.