

THEORY OF CYCLIC VOLTAMMETRY OF GOLD NANOCUSTERS

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Gold nanoclusters (GNCs) have received considerable attention because of their potential for future electronic applications. Cyclic voltammetry (CV) has been a convenient tool for studying GNCs with the analysis typically being based on the Randles equivalent circuit [1]. In this work we present several generalizations of the Randles circuit that better describe the physical interaction between the electrolyte and the GNCs and thereby allow an improved, quantitative understanding of the CV data.

CV data for Au electrodes with attached GNCs encapsulated with alkanethiol (AuC8) and with triethylene oxide (AuEO3) are shown in Fig. 1. Two key features of these data are rectification, i.e., larger current for more positive bias, and quantum charging (QC), i.e., small periodic peaks. Although the Randles circuit can fit the rectification by making the cluster capacitance vary with bias, we find that a modified version of the circuit (Fig. 2, inset) that splits the cluster capacitance into separate electrode and buffer contributions gives a better representation. In particular, we find that the Randles circuit requires an unrealistically small effective dielectric constant (Fig. 2) in order to fit the CV of the AuC8 clusters in Fig. 1 (dotted curves).

The Randles circuit is incapable of providing a physical representation of the QC phenomenon because it does not model *individual* clusters and so cannot describe their charging by single electrons. Of course a direct representation of the clusters is computationally unrealistic since in the experiment there are roughly 10^{13} clusters. We therefore we simulate a scaled version (e.g., with 20 clusters) and, using the orthodox theory of Coulomb blockade [2], obtain CV results like those shown in Fig. 3. In these simulations the ratio between the electronic and ionic time constants has been varied and we find that, when the ratio is small, one observes clear QC peaks whereas for larger ratios these peaks are less discernable. The reason is that fast ionic screening keeps the cluster quasi-neutral and thereby suppresses the blockade. To further analyze such data we Fourier transform it and in Fig. 4 plot the peak (at the frequency corresponding to the QC periodicity in voltage) versus the time constant ratio. That we find a slope of $-1/2$ in the log-log plot shows that the QC peaks are diffusion-limited, specifically by ionic screening. Moreover, if we plot the results from a Fourier analysis of the experimental data we can estimate, via the extrapolation in Fig. 4, the time constant ratios of the AuC8 and AuEO3 clusters. The simplest interpretation of these data is that the tunneling probability of the AuEO3 shell is roughly an order of magnitude larger and it is this that causes the AuEO3 QC peaks to be enhanced (Fig. 1).

At the meeting, our improved picture of the physics, the equivalent circuits, the modeling procedures and various simulation results will be discussed in greater detail.

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2. Wasshuber, C., *Computational Single Electronics*, Springer-Verlag: Vienna, 2001.

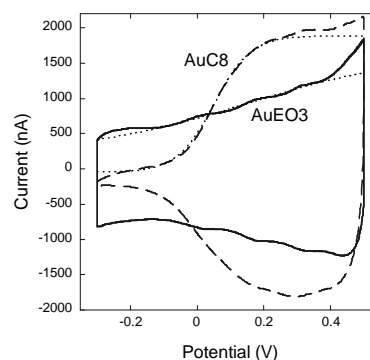


Fig. 1. Experimental CVs for Au electrodes coated with AuEO3 (solid) and AuC8 (dashed) clusters and an NH_4PF_6 electrolyte. The dotted curves are from equivalent circuit modeling.

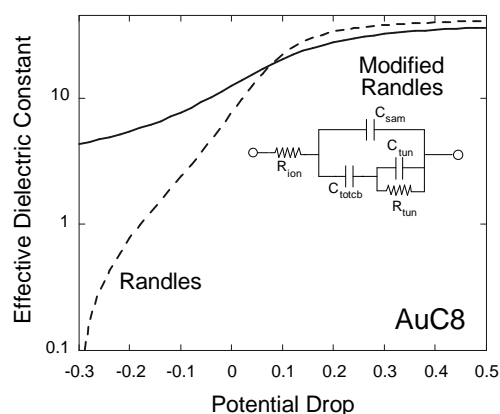


Fig. 2. The dielectric constant of the AuC8 cluster shell as inferred using the Randles and modified Randles (inset) circuits.

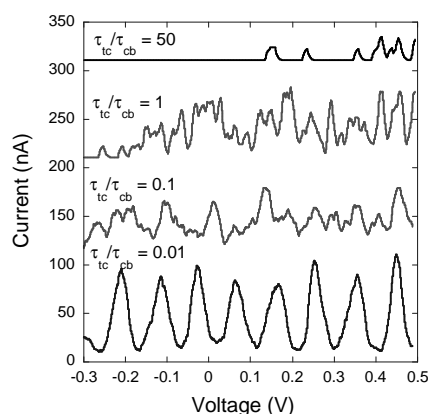


Fig. 3. Simulated LSV curves (with 100nA shifts introduced for clarity) in the Coulomb blockade regime with the ratio between the electronic (τ_{tc}) and ionic (τ_{cb}) time constants varied.

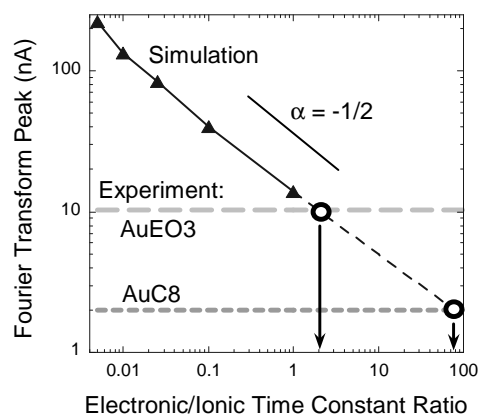


Fig. 4. Fourier peak associated with the QC effect as a function of τ_{tc}/τ_{cb} as simulated (solid) and extrapolated (dashed). The experimental observed values are also shown as well as their estimated time constant ratios.