



Surface area of nanoporous gold: Effect on temperature



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ABSTRACT

Nanoporous Au in two distinctly different surface states, namely, positively charged as-dealloyed and reduced clean metallic were investigated for temperature dependent properties like specific capacitance C_s and specific mass surface area α_m . An electrochemical double layer capacitance ratio method was employed to carry out these studies. It is shown that for reduced clean metallic nanoporous Au sample, the variation in $\ln(C_s)$ versus $1/T$ plot is almost linear, which supports to the negative temperature coefficient predicted by the double layer model. This observation is in direct contrast with positively charged as-dealloyed nanoporous Au that did not reveal any such trend. We compare the specific-mass surface area α_m of nanoporous Au values with the geometrical surface area α_g , obtained by using the “ball-stick geometrical model” coupled with scanning electron microscopy images. Evolution of ultra small nanometric structures during dealloying renders positively charged as-dealloyed nanoporous Au vulnerable to oxidation and ligament coarsening up on its reduction. The validation of the specific-mass surface area obtained from the capacitance ratio method was confirmed by Brunauer-Emmett-Teller analysis and the process of adsorption/desorption of OH adsorbed species on pore surfaces in reduced clean metallic np-Au.

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1. Introduction

The strategies in the design of nanoporous (np-) metals for functional applications depend on a number of parameters. The important ones are surface area, geometry of the pore-ligament interconnects and chemical nature of atom layer present at the pore surfaces and their interaction with surroundings, be it in fluidic or gaseous media. [1,2,3,4]. Among these, the dominant interest has been focused on the surface area of nanoporous metals since their specific surface reactivity depend on the delocalized atom density at the pore surfaces and their co-ordination with the interacting medium. For instance, the electric field induced mechanical actuation effect has been found in nanoporous metals [4–6]. There is also increased grafting density of biological molecules on np-Au [7] and nanoporous surfaces exhibit unexpected catalytic activity [1,4,8,9]. These are few exemplary reports that highlight the importance of surface area and its controlled properties in nanoporous metals.

Electrochemical measurements like electrosorption of hydrogen and oxygen adsorbed atoms [10], under potential deposition (UPD) of metal atoms on foreign substrates [11,12] and Brunauer-

Emmet-Teller (BET) method [13,14] have been used regularly for the determination of surface area in solid materials. Despite the advantages that surface area measurement techniques based on the analysis of adsorption/desorption isotherm, there are difficulties on using these techniques for the determination of true surface area in nanocrystalline metallic materials such as nanoporous metals where the atom diffusivity in the surface layer is quite high at room temperature. The reason is based on the surface diffusion controlled reconstruction rather than a simple atomic displacement, bond breaking, facets and atomic coarsening that occur during heat treatment. STM measurements by Magnussen et al. have revealed that anions chemisorbed with metal electrodes weaken the bond strength between metal atoms and facilitates surface atom transport [15,16]. Liu et al. pointed out that the thickness dependent kinetics of UPD layer formations in nanoporous metals affect the determination of their true surface area [12]. Various other molecular adsorption methods such as carbon monoxide, H_2 and H_2-O_2 titration can also be used to through light on surface area in nanoporous solids. Of all these methods, electrochemistry based techniques offer advantageous as the preparation of the nanoporous samples and the determination of surface area can be carried out at ambient conditions in an electrochemical cell without exposure of the probe samples to other environments. In the backdrop of above, present article

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strives to bring forward a development of an in-situ electrochemical experimental method for determination of surface area of nanoporous metals such as np-Au.

We used electrical double layer (edl) capacitance ratio method [10,17] to study the temperature effect on the variation of surface area in np-Au in two distinct surface states, namely, positively charged as-dealloyed (pcad) and reduced clean metallic (rcm). In the electrochemical double layer interface, the net charge transferred across the electrode surface occurs mostly by the coupled influence of diffusion of ions in the electrolyte and electrostatic forces [18,19]. The potential δE developed at the double layer interface changes linearly with time for a constant current I flow, i.e. $\delta Q = \int I \cdot dt$ and therefore double layer capacitance $C_{dl} = \frac{\delta Q}{\delta E}$ can be expressed as $C_{dl} = \frac{1}{\nu} \frac{\delta Q}{\delta E}$, where ν is the scan rate. It is easily obtained from the analysis of cyclic current I versus potential E scans. Since the important contribution to the double layer charging originates from the electrode surfaces, electrochemical capacitance method determines accurately the surface area of the probed materials from the knowledge of net charge transferred [10,18,19]. In addition to the capacitance ratio method, we determine the surface area of pcad np - Au samples using the standard BET method and the process of adsorption/desorption of OH_{ads} species on pore surfaces in clean metallic np-Au.

2. Experimental

Nanoporous Au, characterized by its solid fraction ~ 25 , which is the ratio of mass densities of the porous region to the Au skeleton fraction, has been prepared by following a standard procedure as described in Ref. [20]. Arc melted alloy ingot with nominal composition $\text{Ag}_{75}\text{Au}_{25}$ homogenized at 800°C in a vacuum-sealed quartz ampoule. This ingot was cold-rolled in to shape the samples. Thin plates of thickness $\sim 200\ \mu\text{m}$ obtained from these samples were annealed at 700°C to remove the frozen stress. It was then electrochemically dealloyed by applying a potential of $0.85\ \text{V}$ versus pseudo Ag/AgCl reference electrode in $1\ \text{M}\ \text{HClO}_4$ electrolyte. During the dealloying process, less noble Ag atoms were

selectively removed from the $\text{Ag}_{75}\text{Au}_{25}$ alloy as Ag^+ ions. This process left behind a skeleton Au with a uniform interpenetrating two-phase microstructure consisting of nanometer sized Au ligaments forming a three-dimensional porous network.

The electrochemical experiments were performed in a commercial potentiostat (PGSTAT 302N, Metrohm Autolab e.v.). The temperature dependent surface area data for np-Au obtained from the capacitance ratio method were compared with its geometrical surface area α_g values determined from “ball-stick geometrical model” proposed originally by Huber et al. [21]. All electrochemical experiments in this study were performed under potential control by using Ag/AgCl pseudo reference wire electrode. There is a shift of $-198\ \text{mV}$ to the standard $\text{Ag}/\text{AgCl}/3\ \text{M}\ \text{KCl}$ electrode and $-398\ \text{mV}$ with respect to the standard hydrogen electrode SHE. The latter study also used the scanning electron microscope SEM (Carl-Zeiss Supra 55) to investigate the evolution of surface morphology of the np-Au samples heat-treated below $363\ \text{K}$ in HClO_4 solution. ImageJ software was used to analyze the SEM images of the np-Au samples from which the ligament size d was obtained by averaging the diameter of fifty selected ligaments.

The temperature dependent electrochemical double layer experiments on pcad np-Au and rcm np-Au samples were carried out in constant current passed anodic/cathodic regions around the cell open circuit potential (OCP) in a temperature interval of $298\text{--}363\ \text{K}$. Open circuit potential is the potential difference that develops in a cell when potential applied to the cell is disconnected. After disconnection, this potential rises because of the difference in the electron energy levels in the electrode and in the electrolyte solution. The temperature was controlled using a bath thermostat having an accuracy of $\pm 0.2\ \text{K}$. To remove the adsorbed species that are retained in the pcad np-Au during the dealloying process and for obtaining characteristic electrochemical features of clean Au surfaces, the pcad np-Au immersed in HClO_4 was potential cycled successively in a wider potential interval, between -0.3 and $0.9\ \text{V}$, at a scan rate of $1\ \text{mV}\ \text{s}^{-1}$.

BET surface area measurements were carried out on pcad np-Au having masses 239 and 400 mg. The nitrogen adsorption/desorption isotherms were recorded on these samples after degassing at

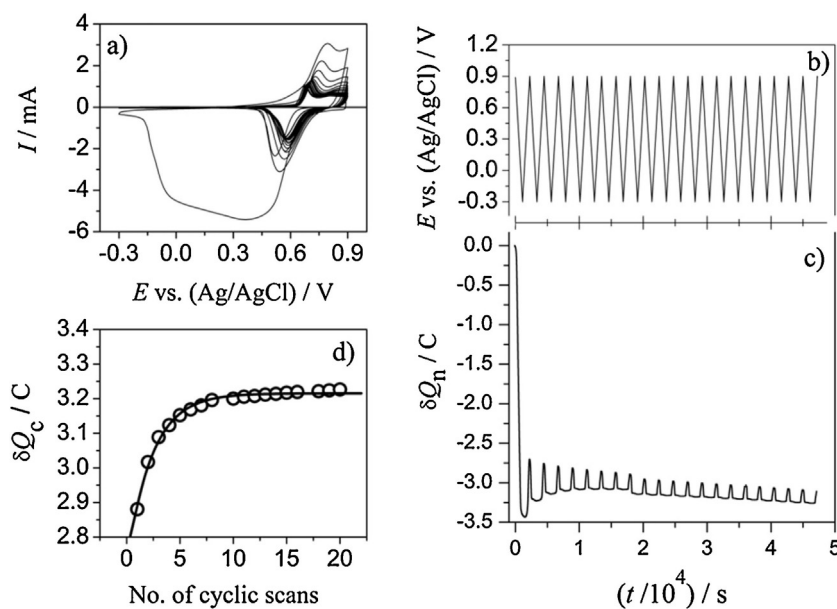


Fig. 1. Results of electrochemical reduction process in positively charged as dealloyed pcad np-Au. (a) Twenty one successive cyclic voltammograms of pcad np-Au recorded in a wider potential interval -0.3 to $0.9\ \text{V}$ at a scan rate of $1\ \text{mV}\ \text{s}^{-1}$. (b), (c) Changes in applied cell potential E versus Ag/AgCl and net charge δQ_n , transferred during the twenty-one successive scans of Fig. (a), respectively. Since the charge δQ_n transferred in the first cathodic scan is much higher the charge values in the subsequent oxidation/reduction scans are not balanced to $\delta Q_n = 0$ in the y-axis. (d) Cumulative charge δQ_c transferred at the end of each successive reduction scan.

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