Electrically Tunable Resistance of a Metal

M. Sagmeister,[1] U. Brossmann,[1] S. Landgraf,[2] and R. Würschum[3,*]

[1]*Institut für Materialphysik, Technische Universität Graz, Petersgasse 16, A-8010 Graz, Austria*
[2]*Institut für Physikalische Chemie, Technische Universität Graz, Technikerstrasse 4, A-8010 Graz, Austria*
[3]*Institut für Materialphysik, Technische Universität Graz, Petersgasse 16, A-8010 Graz, Austria*
(Received 22 December 2005; published 21 April 2006)

Electric field-induced tuning of material properties is usually restricted to nonmetals such as semiconductors and piezoelectric ceramics. We show that variations of the electrical resistance of a metal (Pt) in the range of several percent can be reversibly induced at low charging voltages making use of a nanocrystallite-electrolyte composite. The charge-induced resistance variation is analyzed taking into account the modification of the charge carrier density and scattering rate by surface charging. The contribution arising from the charge-induced variation of the lattice constant is found to be small.

Materials, which change their macroscopic properties, such as the length or electrical conductivity, upon applying an electric field are the focus of basic research and applications. Field-induced tuning of material properties is usually restricted to nonmetals such as semiconductors and piezoelectric ceramics. In bulk metals, no charge-induced changes of such properties are observed. Here, screening due to the high density of conduction electrons limits the extent of space charge regions to the length scale of a few atomic layers.

Although the space-charge regions at metal surfaces are so narrow, changes of a local property, which result from the modified electronic density of states in the space-charge layer, may have an impact on the overall performance of the metal if the surface-to-volume ratio is sufficiently high. This represents the basis of a recent suggestion by Gleiter *et al.* [1] according to which a wide range of properties of nanocrystalline metals may be reversibly tuned by simply adding or withdrawing charges at surfaces through the action of an applied field. Gleiter's concept could recently be demonstrated in a study on porous nanocrystalline platinum by Weissmüller *et al.* [2] where a reversible change of both the lattice spacing and the macroscopic length as an effect of surface charging in an electrochemical cell could be observed. Based on that, the present work aims at studying in how far the electrical resistance of a nanophase metal can be modified by field-induced charging.

A variation of the electrical conductivity in bulk metals has earlier been achieved upon the addition of charge carriers by alloying, e.g., of Pd with Ag [3]. Measurable variations of the electric resistance in metals by applying of electric fields including electrochemical charging have so far been only observed in ultrathin films [4–6]. In the present work porous nanocrystalline bulk Pt is used which should allow efficient charging due to the high surface-to-volume ratio.

The electrical resistance of nanocrystalline metals is controlled by carrier scattering at the crystallite interfaces [7,8]. According to Seeger and Schottky [9] the electrical

resistivity of a grain boundary is correlated to its excess volume. Pt is used in the present study as a model system due to its nearly filled *d* band [10]. While the *d* electrons do not play a significant role as carriers of the electric conduction due to their high effective mass, the density of empty states in the *d* band does determine the scattering rate of the conduction *s* electrons and therefore the electrical resistance [11]. Since the degree of filling of the *d* band is sensitively affected by adding or withdrawing of charge, the carrier scattering at interfaces of nanocrystalline Pt and therefore the electrical resistance is expected to change upon field-induced charging.

Porous nanocrystalline specimens were prepared by gently pressing commercial Pt black (grain size 6–10 nm, purchased from Chempur GmbH, Karlsruhe, Germany) into a $3 \times 4 \times 9$ mm³-sized groove of a Teflon specimen holder. For the resistance measurements 4 Pt wires were embedded as contacts into the specimen material. The specimen assembly was subsequently annealed in vacuum for 12 h at 120 °C in order to obtain a sintered porous network of interconnected nanocrystallites [for picture of microstructure see Ref. [2]]. A mean crystallite size of 10 nm and a specific surface of 21 m²/g were determined by x-ray diffraction and gas adsorption measurements [Brunauer-Emmett-Teller method (BET)], respectively.

The measurements were performed in a standard electrochemical cell at ambient temperature using a potentiostat PGZ-100 (Voltalab Comp.) for charging with the specimen being immersed in an aequeous electrolyte solution of 1-molar KCl. The specimen for resistance measurements served as working electrode (see Fig. 1). A second Pt specimen of similar mass and surface was used as counter electrode and a commercial Ag/AgCl electrode as reference electrode. The dc electrical resistance was measured *in situ* in the cell by means of the 4-point method using a high-precision source- and multimeter Type 2400 (Keithley Comp.).

Charging of the specimen was performed by multistep chrono-amperometric measurements. The voltage applied
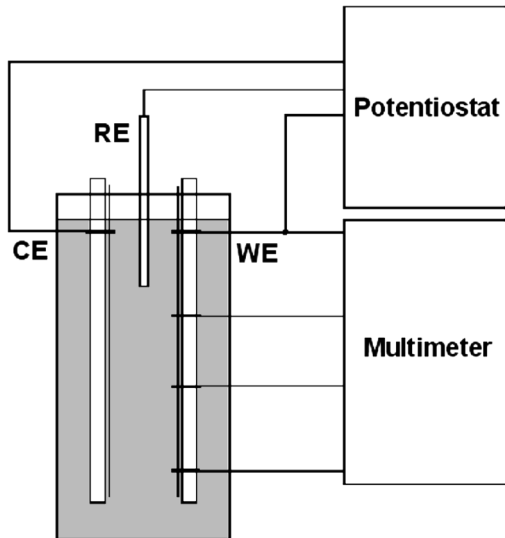
FIG. 1. Electrochemical cell for resistance measurement on porous nanocrystalline Pt by means of 4-point method in dependence of charging by double-layer formation. WE, CE, RE: working, counter, and reference electrode, respectively.
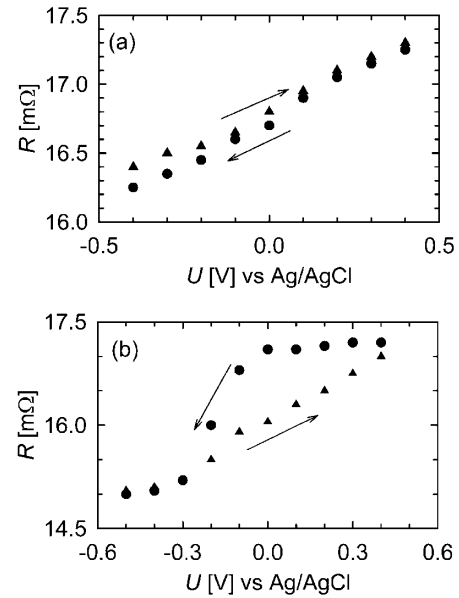

FIG. 2. Variation of the electric resistance R of porous nanocrystalline Pt upon charging with a voltage U using (a) 1-molar KCl or (b) 1-molar KOH as the electrolyte. The arrows indicate the direction of charging.

to the work electrode was incremented in steps of 100 mV at intervals of 30 to 60 min. For each step, the charge quantity was determined by integrating the charging current making a correction for the leak current of about 50 μA. The electrical resistance was recorded simultaneously with a measuring current of 10 mA in order to minimize errors due to the leak current. Data points of the resistance were taken at the end of each charging interval when a constant value was attained. Prior to the measuring run, cyclo-voltammograms with scan rates of 200–500 μV/s were recorded in order to choose the appropriate potential range for charging in the double-layer regime.

Results on electrical resistance (R) measurements in dependence of voltage U used for charging are shown in Fig. 2. Figure 3 depicts the corresponding relative changes of R in dependence of imposed specific surface charge Δq as determined by chrono-amperometry. A key result is the fully reversible and nearly linear variation of the electrical resistance of ca. $\pm 4\%$ upon charging in KCl electrolyte in a voltage range -400 mV to $+400$ mV [Fig. 2(a)] which corresponds to a maximum charge transfer Δq of ca. ± 60 μC/cm^2 (Fig. 3). Adding or removing of electrons gives rise to a decrease or increase of the resistance, respectively. The variation of R is nearly independent of the direction of charging. In addition, essentially the same $\Delta R/R - \Delta q$ relation is observed for different pH values of the electrolyte (Fig. 3). This result shows that the variation of the electrical resistance is indeed due to the imposed surface charge rather than due to chemical effects such as an uptake of hydrogen. This conclusion is further supported by cyclic voltammograms of the porous nanocrystalline Pt specimen as well as by literature data [see, e.g.,

[12]] according to which exclusively double-layer formation occurs in the studied potential range whereas chemical reactions can be excluded.

An influence of chemisorption could, however, be demonstrated in the case of strongly alkaline conditions using 1-molar KOH as electrolyte. Here, a significant hysteresis between the directions of charging occurs [Fig. 2(b)] which is associated with a substantially higher maximum charge
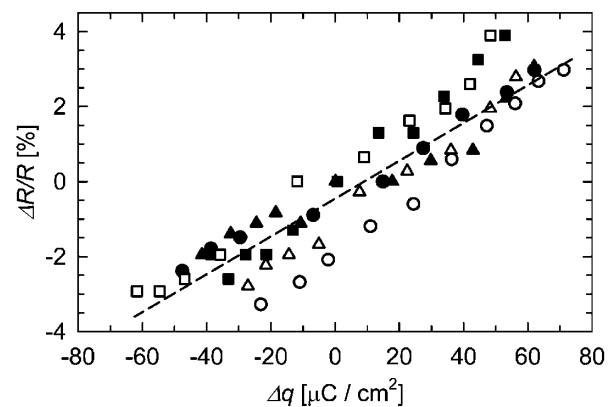

FIG. 3. Relative variation $\Delta R/R$ of the electric resistance of porous nanocrystalline Pt with the imposed specific charge density Δq using KCl as electrolyte with different pH values: 1 M KCl with 0.01-molar KOH (pH 12, $\square$, $\blacksquare$), with 0.01-molar HCl (pH2, $\bullet$, $\circ$), or with a buffer solution of 0.01-molar KH$_2$PO$_4$ and 0.01-molar Na$_2$HPO$_4 \times$ H$_2$O (pH 7, $\triangle$, $\blacktriangle$). Filled and empty symbols refer to charging in positive and negative direction, respectively. The point of zero charging ($\Delta q = 0$) was arbitrarily chosen at zero voltage.

turnover of about ± 6 C but a significantly reduced relative variation of R with Δq. This enhanced charge turnover is due to the formation of Pt-OH and Pt-O at the surface [12] which does not contribute to the voltage-induced space charge in the metal.

Whereas the charge-induced variation of the electrical conduction was found to be reversible within each measurement cycle, a continuous slight decrease of both R and ΔR in consecutive measuring runs occurred. This may result from a progressive slight coarsening of the nanostructure with the measuring time.

In the following, the experimental results of charge-induced resistance variation will be analyzed taking into account (i) the modification of the charge carrier density by surface charging, (ii) the variation of scattering rate of charge carriers at the internal crystallite-electrolyte interface due to charging, and (iii) the effect of a charge-induced variation of the lattice constant.

(i) From the maximum variation of the net charge of ± 1.5 C due to electrochemical double-layer formation a volume-averaged total charge variation of ± 0.025 electrons per atom is estimated for the specimen mass of 120 mg. Related to $0.55–0.6$ electrons per atom in the conduction band of Pt [13], this corresponds to a relative variation of ca. $\pm 4\%$ of the conduction electron density n. Assuming as a most simple approach a Drude model of the electrical conductivity σ with $\sigma \propto n^{2/3}$ [4], an amplitude of the charge-induced variation of σ of ca. $\pm 3\%$ is estimated somewhat less than the value of $\Delta\sigma/\sigma \approx \pm 4\%$ observed experimentally.

In the framework of the Drude model the same relative variation of σ is deduced for the more reasonable assumption that the excess charge which arises from double-layer formation is concentrated at the nanocrystallite-electrolyte interface rather than being uniformly distributed in the nanocrystallites. This follows by describing the interconnected nanocrystallites as a cylindrical nanostructure for which the cylindrical surface shell with a modified carrier density and the cylindrical core act as parallel conduction paths. Assuming that the excess charge is concentrated in the three outmost atomic layers due to the efficient electronic screening, a maximum charge variation of about ± 0.085 electron per atom of this surface shell is estimated from the total charge transfer of ± 1.5 C and the free surface area of 2.5 m^2 as determined from BET.

(ii) Although the predictions of the Drude model of free electrons fairly well agree with the observed charge-induced variation of σ, a more detailed description of the conduction in the Pt nanostructure is required which, on the one hand, takes into account the effect of the unoccupied states of the nearly filled d band of Pt and, on the other hand, the dominant influence of charge carrier scattering at the interfaces of the nanostructure. In fact, for Pt the phonon-induced scattering of the conduction s electrons into the empty states of the d band yields a major contri-

bution of the electrical resistance [[11], see above]. Taking into account that the d band is nearly filled [10], the density of states at the Fermi edge and, therefore, the scattering probability may strongly be modified by varying the degree of filling of the d band upon charging. Since the mean free path of ca. 22 nm of the electrons in crystalline Pt at ambient temperature [11] considerably exceeds the crystallite diameter (ca. 10 nm), the carrier scattering in the nanophase structure predominantly occurs at interfaces, namely, both at the crystal-crystal interfaces (grain boundaries) and at the crystal-electrolyte interfaces. From this consideration it is evident that the electrical resistivity of porous nanocrystalline Pt should sensitively depend on the charge-induced variation of the carrier scattering probability at the crystal-electrolyte interfaces.

For a quantitative assessment we consider the relation $\sigma \propto 1/D_d$ between the conductivity and the density of states D_d at the Fermi edge in the d band of Pt [11]. The variation of D_d at the crystal-electrolyte interfaces due to charging is estimated in the framework of a rigid-band model of the d band. Approximating the energy dependence of D_d at the Fermi edge with a polynomial of second order using the d band parameters of bulk Pt according to Müller *et al.* [10], a variation of D_d of about $\mp 25\%$ upon maximum charging of ± 0.085 electron per atom is estimated. This charge-induced variation of D_d at the crystal-electrolyte interfaces is by about a factor of 6 higher than the variation of σ, which means that only a minor part of the carrier scattering is affected by interface charging. This appears to be reasonable since the internal crystal-crystal interfaces are those which are not affected by double-layer charging but which presumably yield the main contribution to the electrical resistance of nanocrystalline Pt. In addition, the variation of the electron density in the near-surface part of the metallic nanocystallites may be lower than estimated above due to a partial charge transfer to adsorbed ions. Furthermore, an overestimation of charge-induced variation of D_d might arise from the crude underlying assumptions, namely, the rigid-band model and the description of surfaces by the bulk band structure.

(iii) Finally, we will consider the influence of a charge-induced variation of the lattice parameter on the electrical conductivity. This can be done by taking into account literature data of the pressure variation of the resistance of Pd, since Pd and Pt exhibit rather similar electronic and elastic properties. According to Sundquist *et al.* [14] the electrical resistance R of crystalline Pd decreases linearly with pressure with a coefficient $(\Delta R/R)/p = -0.019$ GPa^{-1}. Charging experiments on porous nanocrystalline Pt, on the other hand, which were performed in the same way as in the present work, revealed a reversible compression or dilatation of the lattice upon negative or positive charging [2]. This compression and dilatation was attributed to the interface stress imposed by the surface charge [2]. For a charge transfer corresponding

to the maximum value in our case (60 μC/cm^2) relative variations of the lattice parameter a and the macroscopic length l of 0.018% were found. Taking into account the bulk modulus of Pt and the coefficient $(\Delta R/R)/p$ as given above, this charge-induced variation $\Delta a/a$ or $\Delta l/l$ corresponds to a variation $\Delta R/R$ of the resistance of 0.3%. This shows that the contribution arising from the charge-induced compression and dilatation is small in comparison to the overall charge-induced resistance variation of $\pm 4\%$.

It should be noted that each of the three charge-induced effects discussed above, namely, the variation (i) of the carrier density, (ii) of the scattering probability, and (iii) of the lattice constants gives rise to changes of the conductivity in the same direction. For each of these effects, an excess of negative charge induces an increase of the conductivity and, vice versa, a charge depletion is associated with a decrease of σ.

In comparison to the earlier studies of thin metal films (Au, Ag) which were charged electrostatically by means of an insulating dielectric layer [4,5], the variations of R in the present case are by 3–4 orders of magnitude higher although the voltage applied for charging is by a factor of 10^4 lower. This major advantage of the nanocrystal-electrolyte composite is due to the electrochemically charging by means of double layers [6] which does not require an insulating layer and which, therefore, allows the storage of a high amount of charge at low voltages.

The present concept of charge-induced variation of the electrical resistance of a metal is supported by recent similar studies of the resistance of highly porous graphite used in supercapacitors [15]. Because of the much lower carrier concentration of the half-metal, a substantially higher resistance variation occurred under identical charging conditions in comparison to the present case of porous nanocrystalline Pt.

In summary, a reversible resistance variation of a nanophase metal in the range of several percent upon surface charging was found. Because of the low voltage required for reversible variation of the surface charge density, attractive application potentials, e.g., actuators [2,16], may emerge from the present concept of voltage-induced property tuning of nanophase materials with large surface-to-volume ratio.

---

*Electronic address: wuerschum@tugraz.at

[1] H. Gleiter, J. Weissmüller, O. Wollersheim, and R. Würschum, Acta Mater. **49**, 737 (2001).
[2] J. Weissmüller, R. Viswanath, D. Kramer, P. Zimmer, R. Würschum, and H. Gleiter, Science **300**, 312 (2003).
[3] T. Ricker and E. Pflüger, Z. Metallkd. **57**, 39 (1966).
[4] A. Deubner and K. Rambke, Annalen der Physik **17**, 317 (1956).
[5] G. Bonfiglioli, E. Coen, and R. Malvano, Phys. Rev. **101**, 1281 (1956).
[6] R. Tucceri, Surf. Sci. Rep. **56**, 85 (2004).
[7] R. Birringer, C. Krill, and M. Klingel, Philos. Mag. Lett. **72**, 71 (1995).
[8] J. Vancea, G. Reiss, and H. Hoffmann, Phys. Rev. B **35**, 6435 (1987).
[9] A. Seeger and G. Schottky, Acta Metall. **7**, 495 (1959).
[10] F. Müller, J. Garland, M. Cohen, and K. Bennemann, Ann. Phys. (N.Y.) **67**, 19 (1971).
[11] N. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon, Oxford, 1936).
[12] C. H. Hamann and W. Vielstich, *Elektrochemie* (Wiley VCH, Weinheim, 1998).
[13] P. Bizet and S. Minn, Comptes Rendus de l'Académie des Sciences **286**, 225 (1979).
[14] B. Sundquist, J. Neve, and O. Rapp, Phys. Rev. B **32**, 2200 (1985).
[15] H. Drings, Doctoral thesis, Technische Universität Graz, 2004.
[16] R. Baugham, Science **300**, 286 (2003).