

Magnetization of Fe-oxide based nanocomposite tuned by surface charging

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Aiming at a voltage-control of magnetism, the magnetization of a porous γ -Fe₂O₃-Pt nanocomposite is studied under the influence of charging the surfaces of the porous structure in an electrolyte. Reversible variations of the magnetization of up to 10.4% could be achieved upon charging in the regime

where electrochemical adsorption and desorption occurs. The observed variation of the magnetization with electrochemical charging is assigned to the γ -Fe₂O₃ nanoparticles whereas the conductive network of Pt nanoparticles is necessary for charging.

1 Introduction Switching of magnetism by electric fields has become an important research topic in anticipation of attractive application potentials. The primary focus is on multiferroic materials [1, 2] where magnetoelectric properties arise from the coupling between ferroelectric and ferromagnetic behavior. An alternative niche approach may emerge with the concept of charging of nanocrystalline materials with a high surface-to-volume ratio by means of electrolytes [3]. Upon immersing porous nanocrystalline materials in a liquid electrolyte, high surface charge densities can be achieved at the surface-electrolyte interface. By this way charging-induced reversible variations of the lattice spacing, macroscopic length and electrical resistance as well as of the magnetic properties could be demonstrated [4–7]. For nanocrystalline Pd and Pd-Co alloys charge-induced variations of the magnetic moment in the range of several percents were observed [6, 7]. Subsequently interface charging by means of electrolytes was also applied to ferromagnetic thin films [8]. In the present work this concept of charge-induced property variations is extended to nanocrystalline oxide materials where charging is enabled by means of an oxide metal nanocomposite. Expanding the charging in the regime of electrochemical

surface reactions, reversible variations of the magnetic moment up to 10.4% can be achieved.

2 Experimental γ -Fe₂O₃ nanoparticles with a diameter of ca. 5 nm were prepared by the gas-phase technique of microwave plasma synthesis as described in detail elsewhere [9]. Fe(CO)₅ was used as precursor and a mixture of 80% Ar and 20% O₂ as reaction gas. In order to charge the insulating γ -Fe₂O₃ nanoparticles, a nanocomposite of the oxide nanoparticles and of an interconnected network of Pt nanoparticles was formed. For this purpose the γ -Fe₂O₃ nanoparticles were ultrasonically intermixed with commercial Pt nanoparticles (Chempur, particle diameter 6–10 nm) in a weight ratio of 1:3 and subsequently slightly compacted into a porous specimen with cylindrical shape (diameter 3 mm). For charging the porous specimen was immersed in an aqueous electrolyte of 1 M KOH.

Electrochemical characterization of the porous γ -Fe₂O₃-Pt nanocomposite was performed in a standard electrochemical cell by means of a potentiostat (Autolab PGSTAT128N). The current-voltage characteristic (cyclic voltammogram, CV) is shown in Fig. 1 in comparison to that of a Pt reference sample made from the same Pt

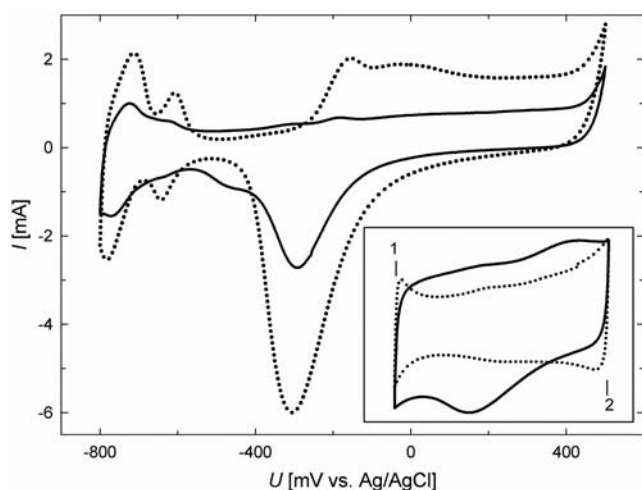


Figure 1 Charging current I versus charging voltage U during cycling at 0.5 mV/s of γ -Fe₂O₃-Pt nanocomposites (solid line) and of nanocrystalline Pt (dotted line). U measured with respect to Ag/AgCl reference electrode. The inset shows CV cycling between -600 mV (1) up to -250 mV (2).

nanoparticles. The Pt sample exhibits the characteristic regimes of chemisorption of oxygen species upon anodic cycling (charging voltage $U > -200$ mV) and subsequent desorption of oxygen species upon cathodic cycling ($U < -300$ mV) as well as the characteristic hydrogen adsorption and desorption peaks ($U < -600$ mV) [10]. In the CV of the γ -Fe₂O₃-Pt nanocomposite additional shoulders at -500 mV in cathodic direction and -300 mV in anodic direction indicate electrochemical surface reactions of the γ -Fe₂O₃ as discussed below (see inset in Fig. 1).

Measurements of the magnetization as a function of charging were performed by means of a SQUID magnetometer at a constant temperature of 300 ± 0.01 K (MPMS-XL-7 instrument, Quantum Design). For this purpose a two-electrode chemical cell was designed which allowed in-situ charging of the γ -Fe₂O₃-Pt nanocomposite specimen in the magnetometer. The porous specimen was mounted in a cylindrical shaped Teflon container (PTFE, outer diameter of 5.5 mm, height ca. 12 mm). The counter electrode of carbon clothing was arranged concentrically at the inner wall of the container and separated electronically from the specimen by a battery separator foil. After filling with the liquid electrolyte, the cell was closed with a Teflon plug and sealed with epoxy resin.

In-situ charging during magnetometry was controlled by a potentiostat in a two-electrode mode (Voltlab 10, Radiometer Analytical). Upon stepwise changing the charging voltage, the charging current was monitored from which the accumulated charge was obtained by integration making a correction for a low residual current. Data points of the magnetic moment were taken at the end of each charging interval when a constant value was attained. The appropriate charging voltage in the two-electrode cell was determined by comparison with reference measurements in the standard three-electrode setup during which simultane-

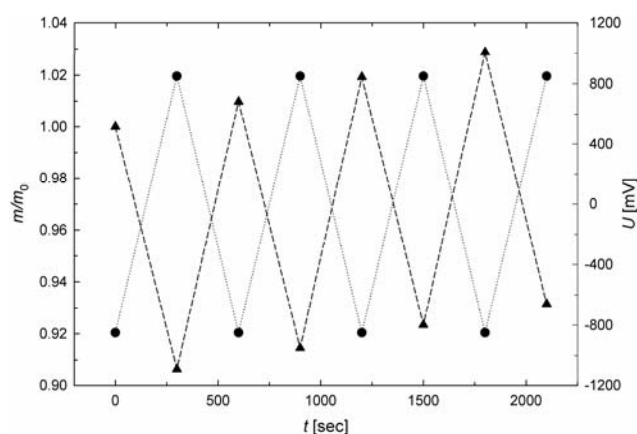


Figure 2 Variation of the magnetic moment m (▲) of γ -Fe₂O₃-Pt nanocomposites with time (t) upon cycling between the charging voltages U (●) at a magnetic field of 50 kOe. Reversible cycling between -850 mV and +850 mV covers the regime of chemical adsorption and desorption. $m_0 = 5.5$ emu g⁻¹ refers to the start of the measuring sequence.

ously the voltages between the working and counter electrode and between the working and reference electrode were monitored. In-situ charging during magnetometry in the two-electrode set-up was performed between -850 mV and +850 mV which corresponds to ca. -550 mV to 0 mV in the standard three-electrode set-up. This voltage range covers the regimes of electrochemical surface reactions of γ -Fe₂O₃.

3 Results Figure 2 shows the variation of the magnetic moment m measured at a field of 50 kOe ($= 3.98$ MA m⁻¹) in response to cycling the charging voltage U in the regime of electrochemical surface reactions between -850 mV and +850 mV. A fully reversible decrease or increase of the magnetic moment upon positive or negative charging occurs, respectively. The relative charge-induced variation $\Delta m/m_0$ of the magnetic moment amounts to 10.4% (Fig. 2). Cycling in the surface reaction regime is associated with an imposed specific charge ΔQ of 62 C g⁻¹. Relating the relative variation $\Delta m/m_0$ to the imposed charge ΔQ , yields a charge coefficient $(\Delta m/m_0)/\Delta Q$ of -1.7×10^{-3} g C⁻¹. A similar value $(\Delta m/m_0)/\Delta Q$ is observed for a second sample with $\Delta m/m_0 = 4.3\%$ for $\Delta Q = 32$ C g⁻¹. The variation $\Delta m/m_0$ is much lower if the cycling is restricted to the pseudo-capacitive regime.

The observed variation of the magnetization with electrochemical charging has to be assigned to the γ -Fe₂O₃ nanoparticles, since the specific magnetization of the γ -Fe₂O₃-Pt composite of 5.5 emu g⁻¹ ($= 5.5 \times 10^{-3}$ Am² g⁻¹ for 50 kOe) is a factor of ca. 70 larger than that of the Pt particles as deduced from the paramagnetic susceptibility of Pt and the magnetic moment measured separately for pure γ -Fe₂O₃. As characteristic for nanoparticles, the measured magnetic moment of 13.5 emu g⁻¹ (for 50 kOe)

of the uncompact γ -Fe₂O₃ nanoparticles is strongly reduced in comparison to bulk crystalline γ -Fe₂O₃ [11].

It can safely be ruled out that the residual charging current significantly affects the charge-induced tuning of m . In fact, reference measurements on carbon cloth as working electrode in the identical cell set-up with a residual cell current $I = 0.2$ mA yields a maximum variation $\Delta m_{\text{ref}} = 1.06 \times 10^{-5}$ emu upon cycling, which is three orders of magnitude lower than that ($\Delta m = 1.16 \times 10^{-2}$ emu) observed for the γ -Fe₂O₃-Pt nanocomposite with $I = 0.75$ mA.

4 Discussion For the discussion of the present results, first of all it has to be pointed out that the charging-induced variation of the magnetization of the γ -Fe₂O₃-Pt nanocomposite of 10.4% is substantially larger in comparison to the few available results on porous nanophase metals where charging was performed in the same manner as in the present study [6, 7, 12, 13]. For ferromagnetic nanocrystalline Pd₉₀Co₁₀, a decrease of the magnetic moment of 3% upon positive charging in the double-layer regime was observed [7]. This variation could not be explained in a simple picture of adding or withdrawing of electrons from the d-band, which in fact should have given rise to the opposite trend, but the charge-induced surface stress was considered as the dominant effect giving rise to the charge-induced tuning of the magnetic moment owing to magnetoelastic coupling [7]. Similarly, in a recent study on nanoporous Au-Fe, a charging-induced variation of the magnetic moment of 0.2% was attributed to surface charge induced pressure as well [13]. For the present γ -Fe₂O₃-Pt nanocomposite, no information on charge-induced surface stress is available and, therefore, no unambiguous conclusion can be drawn to what extent the observed 10% change of the magnetization is affected by magnetostrictive response to surface charges.

Since chemisorption of oxygen species and desorption occurs in the voltage regime of charging, the variation of the magnetization may be related with electrochemically induced reactions at the surface. Literature on such reactions of γ -Fe₂O₃ is rare. According to Jacintho et al., nanoparticles of γ -Fe₂O₃ adsorbed on a silver electrode in an aqueous electrolyte may undergo electrochemical reactions at the surface [14]. The γ -Fe₂O₃ nanoparticles in the aqueous electrolyte are covered by a shell of Fe hydroxides, essentially ferroxylite (δ -FeOOH), which is reduced to magnetite (Fe₃O₄) upon cathodic scan. Fe hydroxides are formed again by reoxidation upon anodic scan [14]. Such kind of surface reaction, i.e., oxidation of Fe₃O₄ to δ -FeOOH upon positive charging, would be in qualitative agreement with the present observation that the magnetic moment decreases with positive charging, because the specific magnetization of δ -FeOOH (<10 emu g⁻¹) is much smaller than that of Fe₃O₄ (90 emu g⁻¹). The additional

shoulders in the cyclovoltammogram of the γ -Fe₂O₃-Pt nanocomposite would also be in qualitative agreement with such kind of surface reaction (Fig. 1, see above).

Although the interpretation of the 10% variation of the magnetization in terms of an electrochemical surface reaction appears to be obvious, other charging effects, like strain, may play a role as well (see above). In any case, the conductive network of Pt nanoparticles is necessary for charging, as futile charging tests without the conductive network have confirmed. This also may indicate, on the other hand, that only the surface parts of the non-conducting γ -Fe₂O₃ nanoparticles which are in close contact with the conduction network of the Pt nanoparticles are affected by charging. Adopting the simple picture of spherical γ -Fe₂O₃ nanoparticles (radius $r = 2.5$ nm) with a surface shell of the thickness of ca. 0.25 nm affected by charging, a volume fraction of 10% would correspond to a fraction of 1/3 of the surface shell. This fraction of 1/3 appears to be quite reasonable showing that a 10% change of magnetization qualitatively may fit with the volume fraction of the γ -Fe₂O₃ nanoparticles which is affected by charging.

5 Summary In summary, it could be demonstrated that the magnetization of γ -Fe₂O₃ nanoparticles can be reversibly tuned by up to 10.4% by means of electrochemical charging via a conductive percolating network. More detailed studies will be necessary, in order to identify more exactly the underlying electrochemical processes. The present concept of tuning of magnetization may open up one promising niche path towards the current challenging efforts of controlling magnetism by electric fields.

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