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Electrode processes and in situ magnetic measurements of FePt films in a $LiPF_6$ based electrolyte

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ABSTRACT

Reversible control of magnetism at the metal/electrolyte interface offers great application potential for multifunctional magnetic devices. Here, the electrode–electrolyte interactions and the charging of FePt alloy films in $LiPF_6$ in dimethyl carbonate(DMC)–ethylene carbonate (EC) are analysed in comparison to the pure metals Fe and Pt. The main electrode processes are Li deposition and dissolution, Fe dissolution and redeposition, and reduction as well as oxidation processes of impurities and electrolyte. Fe is found to be more stable against anodic dissolution in FePt films. Pt attenuates electrode passivation and catalyses impurity reduction reactions. This results in a cathodic potential limit of 1.8 V vs. Li/Li^+ for charging FePt films without side reactions. Subsequently, ultrathin textured FePt films promising large voltage induced magnetic surface effects where used as electrodes. Magnetic properties during charging were monitored by an in situ setup based on the anomalous Hall effect. Marginal Fe dissolution at the surface above 3 V vs. Li/Li^+ is detected by the in situ measurement and limits the upper charging potential. In consequence, a potential window of 1.2 V for charging the FePt films is obtained. In this potential range a large reversible change of magnetic moment is detected, which is attributed to reversible redox processes in the native iron oxide surface layer.

1. Introduction

Reversible property changes at metal surfaces are of great interest for the design of nanoscaled devices with high surface/volume ratio. The electrode/electrolyte interface offers the possibility of tuning the electrode properties by potential dependent reversible electrode processes, including double layer charging, ad- and desorption processes and surface-near reversible redox reactions. They will be shortly addressed below with respect to the change of magnetic properties.

During double layer charging in an electrolyte, an electric field at the electrode surface builds up. This electric field leads to changes of the surface electronic structure [1,2]. Thus, magnetic properties as magnetocrystalline anisotropy and magnetic moment that depend on the electronic structure are expected to change at the surface [3]. First experiments investigating this magnetoelectric effect focused on alloy electrodes consisting of noble metals or transition/noble metal alloys such as Pd [4], FePt and FePd [5], and CoPd [6,7]. Reported changes of magnetic susceptibility (1% in Pd [4]) and coercivity (−4.5% in FePt, 1% in FePd [5]) agree with predictions of first principle calculations [3] within the proposed concept of double layer charging.

At the same time, reversible changes of magnetism at charged electrodes have been reported that point at mechanisms other than the direct magnetoelectric effect by double layer charging [6,7]. Changes of magnetic moment of 3% in CoPd nanoparticles [6] and 4.5% in CoPd films [7] are opposite in sign to the moment change expected from electron theory. Also the additionally observed change of Kerr rotation during charging of FePt [5] still lacks explanation. Due to the complex nature of the electrode/electrolyte interface, various effects have been discussed as origin for the unexpected magnetic property changes. In the potential range of double layer charging and ad-/desorption changes of surface relaxation [8], reconstruction [9], stress [10,11] and strain [12] can occur and may influence the surface magnetic properties. The moment change in the CoPd nanoparticles, e.g., has been related to a magnetoelastic effect resulting from a charge-induced change of the surface stress [6].

An even larger effect on the surface magnetic properties is expected when surface phases are changed. In an electrolyte, phase changes can be achieved by electrochemical reactions. In case of reversibility, these could also be used to reversibly control the

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magnetic properties. One first example related to redox reactions is the change of the magnetic moment in iron oxide nanoparticles [13]. Nakamura et al. [14] suggested that also the variation of the magnetic anisotropy at a charged Fe/MgO interface is due to changes in the iron oxide at the interface.

The above description shows that various processes at the electrode/electrolyte interface may be used to control magnetic properties by an external voltage. However, electrochemical investigations that allow to distinguish between the magnetoelectric effect by double layer charging, indirect effects and redox reactions have only scarcely been carried out. Information on the amount of charge involved and the role of side reactions is required in order to better identify the underlying processes and to optimize them for larger reversible changes.

The present study aims at understanding the interfacial processes at a FePt electrode. For a wide potential window suitable for charging, nonaqueous electrolytes are better suited than aqueous ones as they avoid the hydrogen evolution reaction known to be catalysed by Pt [15]. We selected $LiPF_6$ in the solvent of mixture dimethyl carbonate (DMC) and ethylene carbonate (EC). This electrolyte allows for a high surface charge density and has already been investigated for the use in supercapacitors [16].

In the present study, first the electrode processes of Fe, Pt and FePt in $LiPF_6$ in DMC/EC are analysed by cyclic voltammetry (CV), X-ray photoelectron spectroscopy and atomic force microscopy. The suitable potential window for charging thick FePt films is determined. Next, ultrathin textured FePt films with competing magnetic anisotropies [17] promising a large electric-field induced surface effect are used as electrode. The properties of the film surface in the as-deposited state and after interaction with the electrolyte are investigated by X-ray photoelectron spectroscopy. In situ magnetic measurements in a two-electrode Hall cell are used to identify reversible and irreversible magnetic property changes during charging. The combination of the ex situ and in situ methods enables analyzing the underlying electrochemical processes.

2. Experimental

For the characterization of the electrode processes, a three-electrode electrochemical cell is used. Fe and Pt films (30–200 nm thick, prepared by pulsed laser deposition) on oxidised Si substrates were mounted as working electrode at the bottom of the electrolyte compartment, which is sealed with O-rings with a diameter of 6 mm. Cu wires wrapped by Li metal are used as reference and counter electrodes. All potentials reported are referenced vs. the Li/Li^+ reference electrode ($E^0 = -3.04$ V). The commercial electrolyte LP 30 SelectiLyte from Merck Chemicals containing 1 M $LiPF_6$ in DMC/EC (1:1) with maximum 50 ppm HF and 20 ppm water (manufacturer information) was used as electrolyte. Cell assembly and measurements took place in an Ar glove box. Cyclic voltammograms were conducted using the potentiostat Autolab 302N. The current density is calculated using the electrode area exposed to the electrolyte (28 mm^2). To allow transfer to the in situ two-electrode cell setup described below, besides the potential of the working electrode, the cell voltage (potential between working and counter electrode) has been monitored during the measurements.

For the investigation of the magnetic properties during charging, ultrathin FePt films (2 nm) were prepared by pulsed laser deposition (PLD) in ultra high vacuum (10^{-9} mbar) using an Fe–Pt alloy target. They were deposited on single crystalline MgO(0 0 1) substrates heated to 450 °C and post annealed in the PLD chamber to control FePt $L1_0$ ordering [17]. Prior to the growth of the FePt a Cr(3 nm)/Pt(50 nm) buffer layer was deposited at 300 °C.

Surface morphology of the films was investigated by atomic force microscopy (AFM, Dimension 3100 AFM from Digital Instruments) in tapping mode. X-ray diffraction with Co K_α radiation in Bragg–Brentano geometry was used for structure and texture determination (Philipps XPert PW 3400/00). The chemical states of Pt and Fe were investigated by means of X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out at a PHI 5600 CI (Physical Electronics) spectrometer which is equipped with a hemispherical analyser operated with a typical pass energy of 29 eV. The analysis area had a diameter of approx. 800 μm. Monochromatic Al-Kα excitation (350 W) was used. The information depth of the measurements was varied by changing the angle between analyser and sample surface (values are given with respect to the substrate normal).

To probe the magnetic properties during electrochemical charging, an electrochemical two electrode in situ Hall cell for use in a Physical Property Measurement System (PPMS) magnetometer had been constructed (Fig. 1). For contacting the cell within the PPMS, it is constructed on top of a PPMS puck (1). The sample holder (2) contains the FePt films as working electrode (3). The electrolyte compartment (4) is mounted on top of the sample gets sealed by O-rings (8) during assembly. After filling this compartment with electrolyte (7), the top screw (5) containing the Li counter electrode (6) is screwed on, sealing the cell. The cell is assembled in an Ar glove box. The Hall contacts (9) are realized by press contacts on the sample surface outside the electrolyte area. The counter and working electrodes as well as the Hall contacts are contacted by wires to the electrical contacts located on the puck.

The anomalous Hall effect (AHE) measurements, in contrast to conventional magnetometry, have a favourable scaling behaviour with decreasing film thickness, as sample resistivity increases but magnetic moment decreases. Furthermore, this method is insensitive to the setup of an electrochemical cell, which hinders conventional magnetometry since its para/diamagnetic moments by far exceed the ferromagnetic moment of ultrathin films. In Hall geometry, the applied magnetic field H is perpendicular to the film plane. The applied current I (10 – 100 mA) and the measured Hall voltage $U_{Hall} = R_{Hall} I$ are perpendicular to each other in the film plane (Fig. 1(b). The Hall resistivity R_{Hall} exhibits two contributions in ferromagnets: $R_{Hall} = R_0 H_\perp + R_S M_\perp(H)$ (1) [18]. $R_0 H$ (R_0 - normal Hall coefficient) is the normal Hall resistivity and $R_S M_\perp$ (R_S – anomalous Hall coefficient, $M_\perp$ – perpendicular magnetisation component) is the anomalous Hall resistivity R_{AH}. As the normal Hall effect depends linearly on the applied magnetic field H it can be subtracted using high field measurement data. The resulting anomalous Hall resistivity curve $R_{AH}(H)$ is then correlated to the magnetic hysteresis curve $M_\perp(H)$. Changes in R_S cannot be excluded, but are minimised as the measurements are performed at constant temperature and for the same sample. The changes of R_{AH} are used as approximation for changes in magnetisation. The measurements were performed in a PPMS 6100 from Quantum Design with a maximum field of 9 T. A self-developed software based on Testpoint was used for automated measurements at different magnetic fields and cell voltages.

AHE measurement curves for 2 nm FePt(0 0 1) films are shown exemplarily in Fig. 1(c) in comparison to surface sensitive magnetooptical Kerr effect measurements in polar configuration as used by Weisheit et al. [5]. Both techniques can well represent the sample's magnetic behaviour (described in detail in [17]): Without post annealing, due to the absence of magnetocrystalline anisotropy in the FePt A1 phase, the in-plane shape anisotropy leads to closed hysteresis loops with dominant rotation of the magnetisation (grey lines). Post annealing leads to $L1_0$(0 0 1) phase formation, perpendicular anisotropy and steep hysteresis loops with switching of the magnetisation (black lines). The AHE measurements thus proved to be reliable, probing identical magnetisation behaviour at an even higher signal to noise ratio compared to Kerr magnetometry.