Project: K 104 696

Electrodeposition of special magnetic materials from nonaqueous solutions

Final report

1. Elaboration of the reproducible experiments

As compared to the laboratory experiments in aqueous solutions, the elaboration of the reproducible experiments took an extra efforts. This criterion referred to the electrode materials and the electrochemical cell itself. Besided these factors, the solution purity was also checked but this did not prove to be crucial.

1.a. The working electrode

For the electrodeposition experiments in non-aqueous solutions, we had to develop an electrode configuration that can be used in a reproducible manner for routine experiments. The inexpensive Cu substrate often used for aqueous solutions proved to be inappropriate because of various reasons. First, the lack of H^+ ion the nonaqueous solvents that can reduce the oxides on the Cu surface led to the non-continuous, island-like formation of the deposit. Secondly, the Cu as a cathode material was not inert in the presence of the reduction products of the solvents and hence, the corrosion of the Cu cathode was seen in many cases. The damage of the Cu substrate was obvious and blue/green rust was formed on the Cu surface even if couprous/coupric ions were not present in the solution and the oxidation of Cu was not expected under cathodic conditions.

For these reasons, the following protocol was adopted for the routine application of single-use noble metal cathodes: The Cu sheet was immersed into an alkaline $PdCl_2$ solution and a Pd layer of at least 50 nm thickness was deposited onto the Cu surface. This Pd layer served as a noble metal protecting layer and provided reproducible conditions for electrodeposition of the metals from nonaqueous solutions. The Pd layer did not show any sign of corrosion during the experiments in either of the solvents tested. A few comparative experiments were also performed with Pt sheets as the cathode, and the behavior of the bulk Pt cathode and the Pd-covered Cu sheets was identical.

1.b. The reference electrode

There is no generally accepted reference electrode for solvents other than water. Hence, for reference electrode, a saturated calomel electrode was directly immersed into the non-aqueous solutions. A double-junction type electrode was used in order to minimize both the water leakage of the reference electrode itself and the contamination of the equilibrium system of the reference electrode from the organic solvent. This reference configuration provided a sufficient reproducibility that was detected mostly in connection with the anodic decomposition of the solvent. The solutions were systematically tested with water addition to the impact of the water leakage of the reference system but no impact was found up to a few % of water

1.c. The counter electrode

In most of the experiments, the pursuit was to use the identical metal as the counter electrode that was deposited at the cathod. Nevertheless, in many media, the dissolution of the metal under study could not be detected. Wherever the application of the same metal was not possible, a Pt gauze was used as the counter electrode.

1.d. Cell materials

For mild solvents (e.g., alcohols), plexiglass cells could be used with silicone rubber gaskets. However, for moe aggressive solvents (e.g., acetonytrile) the sealing was much imperfect; hence, beaker-type cell had to be used with an immersed cathode on which the active area was defined with a galvanotechnical scotch tape. The alternative solution was a full-teflon cell with no adhesive bonding and the application of highly resistant O-rings.

1.e. The presence of oxygen and water

In aqueous solutions, the deaeration can be crucial for the correct observation of the cathodic current (oxygen reduction is to be avoided). It was tested for a number of solvents whether the persistent purging with argon modifies either the cathodic current signals observed or the quality of the deposit. It was found for all solvents tested that the ambient condition of the thorough deoxygenation of the solution resulted to essentially the same response. This was attributed to the weak protonation ability of all solvents used, which hindered the oxygen reduction.

Similarly, it was compared whether the presence of oxygen may increase the spontaneous oxydation of the deposits. Since the deposits were rinsed after the end of the experiment in ambient condition, the prevention of the oxidation during the deposition had no impact on the final quality of the deposit.

2. Solutes

The big majority of the salts of magnetic metals are available in a hydrated form. Salts with anions like NO_3^-, SO_4^{2-} and ClO_4^- cannot be annealed for drying because of the decomposition of the salt. Other salts with uncommon anion (e.g., $[N(SO_2CF_3)_2]^-$) are available but their price is still so high that no solution can be made in a sufficient metal ion concentration to obtain a deposit. Therefore, halogenide salts were used in practically all experiments. These salts are available in dry form and also can be dried with annealing. The choice of chloride or bromide compound was mostly verified by the higher solubility of one or the other.

The salt used for supporting electrolyte was adjusted to the salt of the metal of interest concerning the anion. For sake of simplicity, the same anion was used. Typical supporting electrolyte was NH_4Cl, LiCl, NaCl and NaBr.

3. Electrodeposition experiments with alcohols as a solvent

3.1. Deposition of Ni

Ni electrodeposits were obtained from various alcoholic solutions 1. The solvents used included methanol, ethanol, 1,2-propanediol, 1,3-propanediol, and glycerol. In all solvents, the solubility of the ionic compounds allowed us to prepare a 0.1 M NiCl2 + 0.1 M NaCl solution. The conductivity varied two orders of magnitude from 7.7 mS/cm (methanol) to 0.077 mS/cm (glycerol), but even the lowest conductivity was suitable for electrochemical experiments. The cyclic voltammograms indicated that the Ni deposition starts at potentials where the solvent decomposition is already a significant byprocess. Based on these experiments, the current efficiency of the Ni deposition was assessed to fall into the interval of 70 % to 30% (from methanol to glycerol).

The Ni dissolution started at some 300 mV more positive potentials than the onset of the Ni deposition. In this sense, the Ni deposition was similar to that from aqueous solution, where the deposition and dissolution processes take place in well-separated potential intervals.

The cyclic voltammograms obtained for alcoholic solvents could be divided into two types. For the majority of the solvents, Ni dissolution could be observed as a single but wide peak. However, in methanol the Ni dissolution took place in two distinct potential regions. This is a fundamentally new feature of the Ni dissolution, which could not be explained.

Scanning electron microscopy images showed that the Ni deposit was discontinuous for some solvents and deposition potential intervals. The general trend was that the more viscous the solvent and the more positive deposition potential were applied, the less continuous deposits were obtained. The X-ray diffractograms showed that the Ni deposits are slightly textured and contains grains of at most 30-40 nm. The diffraction line positions indicated that the deposits were conformal to pure fcc-Ni on the basis of the lattice distances. This was in agreement with the non-destructive energy-dispersive X-ray (EDX) analysis results. The Ni deposit obtained from methanol was free of any other element.

Concerning the magnetic properties of the Ni deposits, there was no significant difference in the remanence and coercivity of the Ni layers obtained from different solvents and/or at different potentials. Independently of the solvent used, a coercive field of 150-170 Oe was measured for the Ni deposits. This is much higher than the coercivity of well-annealed pure Ni. The difference can be explained with microstructural defects.

3.2. Deposition of Ni alloys from methanol

Fe-Ni alloys could be successfully deposited from methanol. Concerning the Fe to Ni ratio in the deposit, the codeposition process can be classified as being anomalous (which means that the less noble element, here Fe, has a larger mole fraction in the deposit than the corresponding ionic ratio in the solution). The composition diagram was recorded for two deposition potentials. These diagrams indicated that the sample composition was essentially independent of the deposition potential, which is in strong contrast with the deposits obtained from aqueous solutions. At low Fe content (below 50 at.%), the deposits were metallic with blackish appearance. However, at high Fe content the deposit changed significantly after removing from the solution. Due to the corrosive effect of the moisture and oxygen in air, the Fe-rich deposits became brownish, corresponding to the colour of rust. Pulse-plating was also tested with a wide range of period time and duty cycle whether the consistency and compactness of the deposit can be improved; however, these experiments did not lead to deposits better than those obtained with d.c. plating. From methanol, the coercivity of the Ni-Fe deposits were significantly higher than the corresponding samples obtained by conventional aqueous deposition; therefore, the non-aqueous approach could not result in the improvement of the soft magnetic properties of Ni-Fe materials.

Ni-Mn alloys could be produced from methanolic bath with a wide range of Ni concentration. Similarly to Fe-Ni alloys, deposits with Mn content higher than 50 at.% were spontaneously oxidized in air after sample preparation. The line structure of the EDX spectra of these samples was identical to the MnO_2 reference material. A deposition feasibility diagram was constructed in which the axes represented the deposition potential and the $c(Mn^{2+})/\{c(Mn^{2+})+c(Ni^{2+})\}$ ratio, and various areas corresponded to continuous metallic deposits, imperfectly coated substrate with metallic deposit, and oxidized high-Mn content samples (with transition areas, where appropriate). The Mn content of the samples deposited from the same bath is a monotoneous function of the deposition potential. At potentials near the onset of the Ni deposition potential, the deposit contains less than 1 at.% Mn, while the Mn content increases at more negative potentials. X-ray photoelectron spectroscopic study was performed a few Ni-Mn deposits in order to reveal the oxidation state of manganese in the deposits. While the surface of the samples was heavily oxidized (both Ni and Mn), an argon ion sputtering that removed the top 30 nm layer led to much cleaner deposits. The overwhelming majority of Ni was in elemental form, while manganese was present in various oxidation states, including Mn(0), Mn(II), Mn(III) and Mn(IV). Mn(0) accounted for about 1/4 part of the manganese found. Since the solution used for the alloy deposition contained Mn(II) and no oxidation took place in the course of the electrodeposition procedure, it can be assumed that the oxide formation took place dominantly after the deposition process. The magnetization study of the Mn-Ni deposits showed that the coercivity of the samples increases with the Mn content of the deposit; however, the reproducibility of the experiments was not satisfactory due to the variation of the non-metallic fragment of the Mn codeposited with Ni.

Gallium deposition from $GaCl_3$ + NaCl solution in methanol solvent was successful. The deposition potential of Ga was around -800 mV (vs. SCE); i.e., more positive than that of Ni. This is surprising since the difference of the standard potential of the two metal ions/metal systems in aqueous solutions is large and the deposition preference is just the opposite. Concerning the difference in the deposition and dissolution potentials, the Ga deposition process was quasi-reversible, similarly to Ni deposition. The EDX analysis of the deposits confirmed the presence of Ga in the deposits. Since the melting point of Ga is close to room temperature, the alloy formation with the substrate could be detected, which was a dominant process for Cu substrate. It was revealed that the choice of the substrate is crucial in this case.

Pure Ga deposits (i.e., Ga deposited with no alloying element) appeared to be non-metallic but had a whitish surface, indicating the spontaneous oxidation of the deposit in air. Compact deposits were also obtained from mixed Ni-Ga solutions. The X-ray diffractograms showed lines characteristics of Ni only. Ga and Ni did not form an alloy deposit, although they have stable alloy phases and the Ni deposition was possible at more positive potentials than in pure $NiCl_2$ solution. This indicated that the Ga^{3+} ions have some catalytic effect on the deposition of Ni, this effect did not lead to alloy formation.

3.3. Deposition of Co from alcohols

Deposition of Co was performed by using several organic solvents. Since the dissolution of dry $CoCl_2$ was very fast as compared to that of $NiCl_2$, these experiments could be performed relatively easily. Alcohols used in the earlier study of the nickel deposition were used (particularly, methanol, ethanol and ethylene glycol. Interestingly, very smooth and compact Co samples were obtained from ethylene glycol, a solvent that did not prove to be satisfactory for Ni deposition. Based on the magnetic properties, the samples contained metallic cobalt. The magnetization behaviour of the samples is conformal to that of ferromagnetic metals. Nevertheless, the magnetization behavior was not indicative of the presence of non-metallic impurities. The EDX results indicated various elements beside cobalt, mostly oxygen. The oxygen being present can be the result of the oxidation of the fine-grained deposit after removing it from the solution. It was not possible to evidence whether oxygen was present also in the bulk. The XRD study of the samples could not provide unambiguous evidence on the structure of the deposits. This latter observation is partly caused by the very similar lattice distances of the two possible crystalline forms of metallic Co. However, the absence of lines characteristic of Co-oxides can be regarded as weak evidence that the oxygen contamination was dominantly present at the sample surface. As a whole, the deposition of Co from alcohols did not lead to deposits that are fundamentally different from those obtained from aqueous solutions.

4. Electrodeposition of Co with various non-aqueous solvents

Dimethyl formamide (DMF), minethyl sulfoxide (DMSO) and acetonitryle (AN) were all used for Co electrodeposition. While the deposition of Co from DMF and DMSO is often mentioned in the relevant literature, the mechanistic beckground is unclear, and no voltammetric information is available. While in DMF and DMSO the solubility of dry $CoCl_2$ and $CoBr_2$ achieved some 100 mM, in acetonitrile the solubility of CoI_2 was the larges in the presence of NaI (some 5 mM concentration could be achieved).

Despite all our efforts, it was not possible to establish the mechanistic of kinetic beckground of the depositon process. Although the soluts and the solvent were somewhat different, the common features of the experiments verify the treatment of these solutions as one group.

First of all, it was experienced that the voltammograms of the solution gave no firm indication of the metal deposition process. The increase of the cathodic current took place at uncertain potentials either in the presence of absence of the metal salt, and the voltammograms exhibited a very wear reproducibility. It was cross-checked whether the weak reproducibility could be explained with the presence of either O_2 or H_2O but no correlation was found between, e.g., the water content of the solution and the character of the voltammograms. For this reason, the experiments for metal depositon could ba performed only in the galvanostatic mode. Also, it was found that the character of the voltammetric curves, either recorded in a supporting electrolyte or in the presence of the metals salt of interest, was strongly influenced by the prehistory of the electrode. If the voltammetric experiment was previously driven beyond the decomposition potential of the selvents, both the cathodic and anodic part of the voltammogram changed significantly. The changes that occurred due to the solvent decomposition could not be elucidated and hence, reproducible voltammograms for the metal deposition could not be obtained.

We made several attempts to reveal the metal dissolution of these solvents. Co deposited from conventional aqueous solution onto Pt electrode were prepared, and the deposit of known thickness was anodically polarized in DMF, DMSO or AN. The anodic current did not indicate the dissolution of Co, which was a distictive feature of these solvent as compared to alcohols. The lack of the dissolution wave also made it impossible to use cyclic voltammetric experiments for the detection of metal deposition.

Adherence of Co deposits from all theses solvents was weak, whichever type of substrate was used (Pt, Cu or Pd-coated Cu). Hence, the magnetic properties of a few samples could be tested only and no systematic study was possible. The EDX measurements indicated that the contamination originating from the solvent used was always present in the deposit; therefore, pure metals could not be obtained by electrodeposition.

5. Electrodeposition test with organic carbonates

Organic carbonates serve as solvent in many kind of lithium ion battery and are stable enough for the deposition of lithium metal. For this reason, it was expected that deposition of other metals would also be possible from these solvents. Ethylene carbonate, propylene carbonate and dimethyl carbonate were selected as test solvent, mostly because these exhibit the largest dielectric constant, which is a key factor to achieve a sufficient solution concentration with ionic solutes. Propylene carbonate and dimethyl carbonate were used as a pure solvent, while ethylene carbonate (which is solid at room temperature) was mixed with the other carbonates in 50 volume percent ratio. Dry nickel chloride and cobalt chloride were soluble in the solvents up to 0.2 mol/liter concentration, and solutions with sodium chloride as supporting electrolyte in 0.5-0.8 mol/liter concentration could also be prepared. The conductivity of the Me(II)-chloride solutions were comparable with the alkali chloride solutions. In the electrodeposition tests, the wide potential window of the carbonate solvents have been observed, but no electrochemical reaction could be observed in the voltammograms up to the decomposition of the solvents. In simple galvanostatic deposition test, deposits could not be detected for either of the metals tested, and the substrates were always unchanged even in the case when the cathode potential was significantly more negative than the decomposition point of the solvent. Although no test could be performed concerning the structure of the solution and the speciation of the solutes, the work hypothesis for the failure of the deposition of metals with higher valency assumes that the halogenide complexes of the Me(II) ions are very stable that does not make it possible to reduce the metal.

6. Miscellaneous other achievements with the support of the present project

6.1. Magnetic/non-magnetic multilayer films

Electrodeposition and characterization of Fe-Co/Cu multilayers was performed. The major novelty of this work that the optimization of the deposition potential of the Cu layer had to be carried out for each single Fe^{2+} concentrations because of the dependence of the dissolution potential on the Fe content of the magnetic layer. Similarly to all other electrodeposited multilayers, no giant magnetoresistance with oscillating character as a function of the Cu layer thickness could be found. The magnetoresistance increased up to 5% at d(Cu)= 5 nm. The comparison of our data with the earlier literature showed that neglecting the potential optimization of the Cu deposition leads to serious misinterpretations.

In order to make the multilayer electrodepositon more effective, a three-pulse method was tested for Co/Cu multilayers where the Cu layer was thinned with anodic dissolution after the usual two-pulse deposition of the Co and Cu layer. It was found that the partial dissolution of the Cu layer leads to a different sample character than the normal two-pulse deposition at equal thickness of the Cu layer. Namely, samples with giant magnetoresistance can be produced with the three-pulse method at such small Cu layer thicknesses that always show anisotropic magnetoresistance when produced with the two-pulse method. Although the magnetoresistance of the three-pulse plated multilayer was high, their structure was less ordered than that of the two-pulse plated sample, which was evidenced by the absence of the satellite peaks on the X-ray diffractograms.

The giant magnetoresistance (GMR) and structure was investigated for electrodeposited Co/Cu multilayers prepared by a conventional galvanostatic/potentiostatic pulse combination from a pure sulfate electrolyte with various layer thicknesses, total multilayer thickness and Cu deposition potential. XRD measurements revealed superlattice satellite reflections for many of the multilayers having sufficiently large thickness (at least 2 nm) of both constituent layers. The observed GMR was found to be dominated by the multilayer-like ferromagnetic contribution even for multilayers without visible superlattice satellites. All relevant parameters measured indicated a complete decoupling of magnetic layers for large spacer thicknesses. For multilayers with Cu layers deposited at more and more positive potentials, the ferromagnetic GMR contribution increased. At the same time, a corresponding reduction of surface roughness measured with atomic force microscopy indicated an improvement of the multilayer structural quality which was, however, not accompanied by an increase of the superlattice reflection intensities. The present results underline that whereas the structural quality as characterized by the surface roughness generally correlates fairly well with the magnitude of the GMR, the microstructural features determining the amplitude of superlattice reflections apparently do not have a direct influence on the GMR.

The impact of various metallic additives on the electrodeposition of Co/Cu multilayers have been tested. The idea of using metallic additives as surfactant comes from the experience of physical depositon experiments (sputtering, evaporation and molecular beam epitaxy). In these experiments, a monoatomic layer of foreign metal such as Pb, Bi, Ag or Au may facilitate the deposition of one metal layer onto the other (i.e., Co on Cu or vica versa) by decreasing the nucleation barrier and to eliminate the stress effect originating form the difference in the lattice distances. In these physical deposition experiments, the monoatomic additive layer behaved as a floating adlayer and did not incorporate into the Co/Cu multilayer. For modelling this surfactant effect, we elaborated galvanic baths containing Pb^{2+} or Ag^{+} that are also suitable for electrodeposition of Co/Cu multilayers. The key factor of the bath composition optimization was the solubility of the additive metal salts and the choice of the appropriate anion. Structure and magnetoresistance of Co/Cu(Pb) and Co/Pb(Ag) multilayers have been tested. It was found that the foreign metal atoms do not facilitate the layer structure formation but behave as structure-breaking components.

The magnetic properties and the magnetoresistance behavior were investigated for electrodeposited nanoscale Co films, Co/Cu/Co sandwiches and Co/Cu multilayers with individual Co layer thicknesses ranging from 1 nm to 20 nm. The measured saturation magnetization values supported reasonably the validity of the nominal layer thicknesses. All three types of layered structure exhibited anisotropic magnetoresistance for thick magnetic layers whereas the Co/Cu/Co sandwiches and Co/Cu multilayers with thinner magnetic layers exhibited giant magnetoresistance (GMR), the GMR magnitude being the largest for the thinnest Co layers. The decreasing values of the relative remanence and the coercive field when reducing the Co layer thickness down to below about 3 nm indicated the presence of superparamagnetic (SPM) regions in the magnetic layers which could be also evidenced for these samples by a decomposition of the magnetoresistance vs. field curves into a ferromagnetic and an SPM contribution. For thicker magnetic layers, the dependence of the coercivity (H_c) on magnetic layer thickness (d) could be described for each of the layered structure types by the usual equation $H_c = H_{co} + a/d^n$ with an exponent around $n = 1$. The common value of n suggests a similar mechanism for the magnetization reversal by domain wall motion in all three structure types and hints, at the same time, for the absence of coupling between magnetic layers in the Co/Cu/Co sandwiches and Co/Cu multilayers.

6.2. Microstructure of Ni electrodeposited in the presence of various grain refiners

The effect of organic additives (saccharin and formic acid) on the microstructure of electrodeposited Ni films was investigated by X-ray diffraction line profile analysis and transmission electron microscopy. In the film deposited without additives, a columnar structure was observedthat is typical for d.c. deposits and also corresponds to a zone in the general layer growth models (the so-called T-zone). Both formic acid and saccharin additives resulted in equiaxed grains with reduced size, as well as increased dislocation and twin fault densities in the nanocrystalline films. Moreover, the structure became homogeneous and free of texture within the total film thickness due to the additives. Saccharin yielded smaller grain size and larger defect density than formic acid. A detailed analysis of the grain size and twin boundary spacing distributions was also carried out with the complementary application of TEM and XRD. Special emphasis was put on distinguishing between the grain size as derived directly from TEM studies and the size of the coherently scattering regions (termed as crystallite size) revealed by XRD. This study was unique in the sense that two advanced structure analysis methods were first applied in parallel for electrodeposited samples.

6.3. Template preparation, nanowire deposition into templates and their properties

A workstation for nanoporous alumina membrane preparation was built by using a recirculating cryostat and thermostated electrochemical cells. The preparation of nanoporous alumina membraned included the electropolishing of high-purity aluminum followed by a mild anodization that lead to an ordered pore system formation. This procedure is fairly well described in the relevant literature.

It was revealed that the initial electropolishing treatment of the Al sample leads to a sensitization of the near-edge zone of the Al disk. This sensitization takes place as a result of the mass and heat transport limitation in the near-edge zone and manifest itself as round-shaped overetched spots near the sample perimeter. During the preparation of the nanoporous membrane, these sensitive zones have to be excluded from the anodized areas. Also, the anodization of Al in oxalic acid at 0 ‘C often led to a partial oxidation of the surface only. However, anodization at 10 ‘C was successful in practically all cases.

The strategy for pore opening after the preparation of the membrane included the fill-up of the pores with naphthalene/heptane solutions by blocking the pores with a non-polar deposit (e.g., naphthalene) and then removing the barrier layer with an aqueous solution of phosphoric acid. This was expected to result in a controlled pore opening without pore widening. Naphthalene was sublimed later, leaving behind the intact pore system as it was formed during the anodization. However, the structure left behind this procedure was still contaminated with organic compounds (a very strong carbon signal was detected in the EDX) and these residues prevented the phosphoric acid to act as a pore opening agent uniformly at the surface. Therefore, the usual phosphoric acid method was used for pore opening, which was also combined with an electrochemical indication method to follow the pore opening process.

Diffusion measurements have been performed with the home-prepared nanoporous alumina membranes. The transport of KCl from one side of the membrane to the other one was followed with conductometric measurement. It was found that the apparent diffusivity of the salt through the membrane was half an order of magnitude smaller than that expected from the literature data of the diffusion coefficient of the same salt as determined in bulk solutions with no geometrical constraints at the nanoscale. These experiments make the first step towards an in-situ membrane check method that makes it possible to design the electrodeposited nanowires with composition modulation at a high accuracy.

Electrodeposited multilayered Ni-Co/Cu nanowires were produced in porous anodic aluminium-oxide template for the comparison of their magnetothermopower and magnetoresistance. The optimization of the deposition process was performed in accord with the method developed in our research group. A clear multilayer structure was obtained for Cu layers thicker than 0.9 nm, which was confirmed with transmission electron microscopy observations. The measurements of both the magnetothermopower and the giant magnetoresistance were performed on individual nanowires. The magnetoresistance measured for a single nanowire was in good agreement with the macroscopic measurement on a bunch of nanowires in the template. In the temperature dependent measurements, a linear dependence between thermopower and conductivity of the nanowires (with the magnetic field as an implicit variable) was found over a wide temperature range (50 K to 325 K). Later, thermoelectric (TE) measurements have been performed on the same nanowires as a function of both the temperature and the external magnetic field. The temperature-dependent (50 K - 300 K) and magnetic field-dependent (up to 1 T) TE power factor (PF) has been determined for homogeneous nanowires with varying Co:Ni ratios as well as for Co-Ni/Cu multilayered nanowires with various Cu layer thicknesses. A systematic investigation of the resistivity, ρ, as well as the Seebeck coefficient, S, was performed for Co-Ni alloy nanowires exhibiting AMR and Co-Ni/Cu multilayered nanowires exhibiting GMR. At room temperature, measured values of TE PFs up to 3.6 $\mathrm{mWK^{-2}m^{-1}}$ for AMR samples and 2.0 $\mathrm{mWK^{-2}m^{-1}}$ for GMR nanowires were obtained. Furthermore, the TE PF was found to increase by up to 13.1 % for AMR Co-Ni alloy nanowires and by up to 52 % for GMR Co-Ni/Cu samples in an external applied magnetic field. According to these measurements, the magnetic nanowires exhibit TE PFs that are of the same order of magnitude as TE PFs of Bi-Sb-Se-Te based thermoelectric materials. These results give the opportunity to adjust the TE power output to changing loads and hot spots through external magnetic fields. This approach is a new direction in the application of multilayered magnetic/non-magnetic nanostructures, too.

6. 4. Theoretical aspects of the layers with mixed conductivity formed on electrodes

In many organic solvents like organic carbonates, the cathode process related to Li deposition or Li intercalation into carbon-type materials is preceded by the formation of a polymeric layer called Solid Electrolyte Interface (SEI). This layer cannot be produced ex-situ (i.e., independently of the electrochemical process); hence, it cannot be studied separately either. This layer is assumed to exhibit a mixed (electrical and ionic) conductivity. The electrochemical behavior of such a layer is hence determined by both types of conductivity. In spite of the importance of this layer in the functionality of the cathode, the direct current behavior of the system does not show any essential information on the SEI. Nevertheless, the alternating current behavior of the system is strongly influenced by the SEI. The various approaches to the AC behavior of the SEI have been summarized and a model is outlined that is capable of separating the ionic and electrical conductivities of the SEI, without including any heuristic element in the equivalent circuit of the system. It has been shown that with the separation of the ionic and electrical conductivity to independent conduction channels, the number of the time constants of the model system becomes equal to that measured for real samples.

6. 5. Electrodeposited supercapacitor materials

High-performance RuO_2 electrodes using a simple pulse electrodeposition method and two different precursors; namely, ruthenium (III) nitrosylsulfate (RuNS) and ruthenium trichloride ($RuCl_3$) have been prepared. RuO_2 has been deposited for the first time through pulsed potential mode at different potentials and deposit time using ruthenium (III) nitrosylsulfate. The coatings were subjected to electrochemical (CV, impedance and charge/discharge) and material characterization (FE-SEM, XRD, TEM and XPS). The RuNS-RuO_2 coating exhibited excellent specific capacitance (1724 F/g at 5 A/g) with remarkable rate capability. This value is significantly higher (52%) than the value obtained for $RuCl_3$-RuO_2 electrode material at 5A/g. The findings provide valuable information on the potential application of RuNS as a precursor for synthesizing RuO_2 and pulse electrodeposition process to produce electrodes for supercapacitors.

7. Summary

The key concept of the project was the replacement of water as solvent during the deposition of magnetic metals that are sensitive to moisture and can easily corrode. The group of alternative solvents ranged to a variety of polar organic liquids, but at the same time, the extremely expensive ionic liquids were excluded. According to the original concept, the elucidation of the electrochemical processes in these solvents combined with the easy recovery of the pure solvents by distillation might lead to new and industrially feasible methods. The original concept of the project could be partly fulfilled. For alcohols, the elucidation of the electrochemical phenomena and the sample preparation were both successful. However, for the big majority of other solvents, the electrochemical (mostly voltammetric) data did not prove to be reproducible and hence, it was not possible to make the desired progress in understanding. Also, the recovery of the solvents was more difficult than expected since some metal salts were too volatile when the solvent was distilled. Based ont he conductometric test of the redistilled solvents, their purity was much inferior to the clean solvent, indicating the insufficient separation of the electrolytes.

Besides, the project was successful in a wide range of fields based on electrochemical deposition of metals and the study of the resulting nanostructures.

8. Miscellaneous achievements

In excess to the publications listed as journal papers, the following outcome could be achieved with the help of the present project:

Publication still pending at the time of the report submission: 1

> (Pulse-plated RuO_2 electrodes of high rate capability for demanding supercapacitor applications; submitted to: Journal of Solid State Electrochemistry)

Lectures presented at international conferences: 3

> (5th European Pulse Plating Seminar, Baden, Austria, 2014; 10th International Workshop on Electrodeposited Nanostructures, Oberwesel am Rhein, Germany, 2014; 5th Regional Symposium on Electrochemistry – South-East Europe, Pravets, Bulgaria, 2015)

Posters presented at international meetings: 7

> (Spring Meeting of the European Materials Research Society (EMRS), Lille, France, 2015; 5th Regional Symposium on Electrochemistry – South-East Europe, Pravets, Bulgaria, 2015; 12th Multinational Congress on Microscopy, Eger, Hungary, 2015; 11th International Workshop on Electrodeposited Nanostructures (EDNANO-11), Balatonfüred, Hungary, 2015)

Theses: 2

> (Ildikó Nagy and Ádám Marsai, BSc, chemistry major, Eötvös University of Budapest, 2015)

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