Investigation of the Stability of Cobalt-Iron Electrodeposition Solutions Containing Di-Ammonium Citrate

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Ammonium citrate has been used as a stabilizing agent in electrodeposition baths for soft magnetic cobalt-iron alloys. The long term stability of these solutions is studied using UV-visible light spectroscopy and x-ray photoelectron spectroscopy (XPS). Solutions containing dibasic ammonium citrate exhibit color changes over time and the eventual formation of precipitates. The change in color is attributed to the oxidation of Fe(II) to Fe(III) by dissolved oxygen, and the precipitates were identified as β-FeO(OH) (akaganeite) and Fe_3O_4 (magnetite). These effects are exacerbated by heating and/or the application of a voltage across the solution. Solution degradation can be significantly delayed by storing in sealed containers, which eliminates exposure to atmospheric oxygen.

Keywords: *Cobalt-iron electrodeposition, alloy electrodeposition, citrate electrolyte, magnetic applications*

Introduction

Hard-disk drives (HDDs) are the major means of non-volatile data storage in most electronic devices. HDDs operate by imprinting bits of data onto rapidly spinning platter material using a strong magnetic field originating at the HDD write-head. To fulfill its role properly, the HDD write-head must possess a soft magnetic core material that is capable of producing strong magnetic fields, while retaining the ability to switch the direction of magnetization quickly and easily. Magnetic write-heads thus require a core material with a high saturation flux density (high magnetic flux per unit area), low coercivity (low resistance to demagnetization), near zero magnetostriction (negligible shape change during magnetization), high permeability (high ability to support the formation of a magnetic field) and the material must be capable of being electrodeposited as a uniform and cohesive thin film, which is currently the standard method of HDD manufacturing.[1] Traditionally these demands have been met by iron-nickel alloys; originally by Permalloy (Ni80-Fe20) and later by the more iron-rich Fe55-Ni45.[1] The demand for ever increasing data storage densities, however, has necessitated that HDDs be capable of writing at higher frequencies on increasingly coercive platter materials.

An attractive alternative to iron-nickel alloys, and one that has been extensively researched, is iron-cobalt alloys. These alloys have been shown to be capable of attaining high saturation flux densities (~2.4T) and can be easily deposited through electrodeposition.[2-4] Iron-cobalt alloys typically suffer from higher coercivities than iron-nickel alloys, but through careful control of the compositional and morphological characteristics of the deposits, the coercivity can be reduced. Numerous studies have demonstrated that the best combination of magnetic properties for iron-cobalt thin film deposits require the formation of nano-sized grains.

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This has previously been accomplished through the codeposition of BCC and FCC phases, which limits grain size due to competitive growth.

Iron-cobalt electrodeposition solutions have long-term stability issues due to their tendency to form iron hydroxide precipitates, which can also be incorporated into deposits and adversely affect their magnetic properties.[4] The low solubility of $Fe(OH)_3$ means that it is easily precipitated out in the slightly higher pH region next to the cathode. Since the iron ions are added to the electrodeposition solution as an Fe(II) salt, the presence of $Fe(OH)_3$ indicates that the oxidation of Fe(II) to Fe(III) cations has occurred. This was confirmed by assays for Fe(II) and Fe(III) performed on the solution both before and after it was used.[4] The assay showed that the Fe(III)/[Fe(II) + Fe(III)] ratio increased from 0.5 to 3.11 after the solution was utilized for electrodeposition. The solution stability can be improved by lowering its pH (typically to 2.0 - 3.0) to reduce the concentration of hydroxyl ions. Lowering the pH, however, has the undesirable effect of producing voids in the deposits as a consequence of hydrogen evolution at the cathode during electrodeposition.[5] One alternative is to use additives, such as ammonium citrate, to extend the useful lifetime of electrodeposition solutions without the necessity of reducing the pH of the solutions,[6,7] *i.e.*, the solution can be used at its natural pH. Ammonium citrate complexes with iron ions so that the pH at which $Fe(OH)_3$ forms increases from ~3 to almost 6 (for a 0.395M concentration of citrate added to a solution with 0.08M $CoSO_4$, 0.015M $FeSO_4$ and 0.3M $NiSO_4$).[6,7] Trimethylamineborane (TMAB) is another additive which can suppress Fe(III) formation, and increase the magnetic saturation flux density of iron-cobalt deposits (from 2.0 to 2.3T).[4] Another method involves the physical separation of the anode from the electrodeposition solution by using a dual cell. In this configuration, the cathode is immersed in the solution and is electrically connected to the anode, which is immersed in a separate solution, via a salt bridge. Using this method, magnetic saturation flux densities of 2.4T were achieved along with coercivities as low as 6.0 Oe (through additional processing modifications).[8]

In this work, the long term stability of an iron-cobalt electrodeposition solution, containing sulfate salts of the metals and dibasic ammonium citrate as a stabilizing additive, is investigated. UV-visible optical spectroscopy and x-ray photoelectron spectroscopy (XPS) are utilized to study the solutions and any precipitates.

Experimental procedure

The composition of the standard citrate-stabilized electrodeposition solution that was analyzed is shown in Table 1. This composition is based on previous work.[7] Variations on this standard solution were used in several experiments. For example, some solutions were prepared without either $CoSO_4{\cdot}7H_2O$ or $FeSO_4{\cdot}7H_2O$ or with $FeNH_4(SO_2)_2{\cdot}12H_2O$ substituted for $FeSO_4{\cdot}7H_2O$. Electrodeposition was done using fresh solutions and pulsed current (6 msec on-time and 4 msec off-time) with an average current density of 15 mA/cm^2 for 9 min. These conditions produced deposits containing ~68% Co and ~22% Fe with a thickness of 1.7 µm. The cathode consisted of a diced section of a titanium (100 nm)/gold (500 nm) metallized silicon wafer. A diced section of a titanium (75 nm)/platinum (200 nm)-metallized silicon wafer was used as the anode. The metals were sputter deposited onto the silicon substrates, the titanium acting as an adhesion layer upon which the gold or platinum was deposited. Current was supplied using a Dynatronix, Inc. (Model DuPR10-.1-.3) power supply.

Table 1
Composition of standard solution

Reagent	Concentration
$CoSO_4{\cdot}7H_2O$	0.12 mol/L
$FeSO_4 \cdot 7H_2O$	0.048 mol/L
H_3BO_3	0.4 mol/L
Sodium lauryl sulfate $CH_3(CH_2)_{11}OSO_3Na$	0.01 g/L
Dibasic ammonium citrate $(NH_4)_2HC_6H_5O_7$	4.65 g/L

The stability of the iron-cobalt solutions was determined by measuring the solution pH and the light absorbance spectra of the solutions. The pH was measured using an Accumet Basic pH meter (Model AB15). The absorbance spectrum for the solutions was measured using a Jenway 6405 UV/Vis spectrophotometer for wavelengths of light between 300 nm and 600 nm with a step size of 1 nm. The absorption baseline was initially calibrated using an optically transparent quartz cell containing deionized water. The cell was rinsed several times with deionized water between samples.

Precipitates generated in the solutions were characterized with a Kratos Axis 165 XPS system, with a monochromatic aluminum Kα x-ray source (1486.6 eV) operated at 210 W. A survey scan in the binding energy range of 0 - 1100 eV was recorded with an analyzer pass energy of 160 eV and a step size of 0.3 eV to identify the elements. This was followed by acquisition of high-resolution spectra (20 eV pass energy and a step size of 0.1 eV) around the elemental peaks of interest, *i.e.*, oxygen (O) and iron (Fe). The number of scans for high resolution spectra was determined according to the spectrum intensities of the elements to be analyzed. The XPS spectra were fitted and deconvoluted using Casa XPS software. The background model was obtained using a

Shirley algorithm and the individual peaks were fitted with Gaussian-Lorentzian line-shapes. Sample charging was compensated for by taking the carbon 1s peak (284.65 eV) as an internal standard.

Results and discussion

Long term stability of dibasic ammonium citrate stabilized solutions

The addition of ammonium citrate was reported to increase greatly the short term stability (<30 days) of iron-cobalt electrodeposition solutions by complexing metal cations, particularly Fe(II) and preventing them from forming hydroxide precipitates.[6,7] Experiments using the solution composition in Table 1 showed that the presence of ammonium citrate does indeed prevent the immediate formation of precipitates from the solution. Electrodeposition solutions, without ammonium citrate as a stabilizer, at their natural pH however formed visible precipitates after only one hour. Under careful observation however, a detectable color change from the original pink to an orange hue was observed when the dibasic ammonium citrate stabilized solutions were left unused and exposed to air for several days. Although faint at first, the color change was visually detectable after only one day of storage and was first noticeable at the solution-atmosphere interface. This color change progressed deeper into the solution as the aging time of the solution was extended. After several months, the solution turned to a deep red color and became murky, indicating the formation of very fine, mostly suspended precipitates. A photograph comparing the fresh standard solution to solutions which had been aged for various lengths of time is shown in Fig. 1.

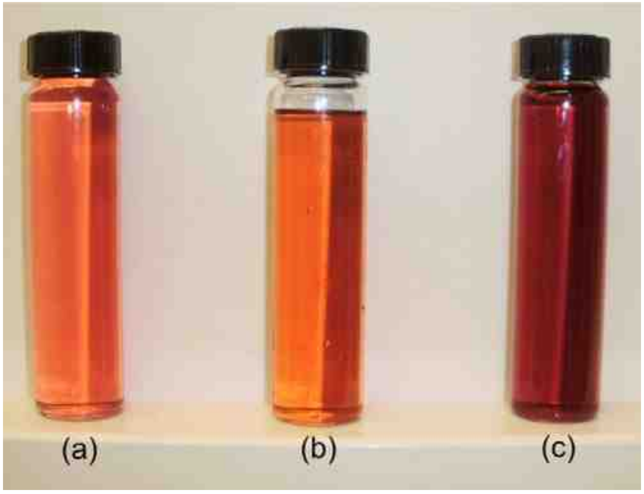

Figure 1 - Standard iron-cobalt solutions, which were exposed to air, in both fresh and aged forms: (a) fresh solution, (b) aged 14 days and (c) aged for more than one year.

UV-visible light absorbance spectroscopy verified the color change as the solution was aged for extended periods of time. Figure 2 shows the absorbance spectra for the iron-cobalt solution, with dibasic ammonium citrate, after various time intervals. The absorption spectrum for the fresh solution shows that light is strongly absorbed at wavelengths from 300 to ~340 nm. At wavelengths higher than ~340 nm, the solution absorbs increasingly less light and reaches a local minimum at ~425 nm. There is a second range of increased absorbance between ~425 nm and ~550 nm, with a peak at ~515 nm. Above this value, the absorbance by the solution is negligible. Moderate aging of the solution has the effect of increasing the lower wavelength range where the solution strongly absorbs light from 300 - 340 nm to 300 - 360 nm. This effect was observed after only one day of aging and did not progress as the solution was aged for longer times. In addition, instead of the solution gradually absorbing less light at wavelengths larger than the range for high absorbance, aged solutions showed a sharp decrease in absorbance at ~360 nm but the absorbance leveled off at a value roughly 60% of the absorbance scale maximum before continuing to fall. The width of the second level of the absorption range was related to the aging time of the solution, with older solutions absorbing a larger range of wavelengths at this level before continuing to drop. As the solution was aged, a new peak at 450 nm was produced, the height of which increased with aging time. The peak at ~515 nm, which was observed in the fresh solution, did not change upon aging in solutions which were aged for up to nine days. When aged for several months, the level region, which started at ~360 nm, was greatly extended to higher wavelengths. This effect was strongly associated with the appearance of precipitates in the solution.

The influence of the individual cationic species, *i.e.*, Co(II) and Fe(II), on the absorption spectra of the iron-cobalt solution was evaluated by analyzing separate solutions containing only one of the two cationic species. The UV-visible light spectra from a solution containing only cobalt cations is shown in Fig. 3. Unlike the iron-cobalt solution, the solution containing only cobalt cations showed very little absorption of low wavelength light. A small peak at ~390 nm is present, but is negligible compared with the absorption at this wavelength in the iron-cobalt solution. The only major peak over the tested range has a maximum at ~515 nm, which corresponds with the high wavelength peak observed in the iron-cobalt solution. There was no change in the absorption spectra as the solution was aged. Visual examination of the solutions also showed no change in the solution color after aging.

The absorption spectra for solutions containing only iron cations are shown in Fig. 4. The absorption spectra for the iron solution show all the aging characteristics observed in the iron-cobalt solution. The fresh iron solution absorbs low wavelength light strongly, but at wavelengths greater than

~325 nm, the absorbance gradually decreases until almost no light is absorbed past ~450 nm. After aging for one day or more, the lower range over which light is intensely absorbed extends to ~360 nm. The spectrum also shows an abrupt drop in absorbance past ~360 nm to ~60% of the maximum absorption scale. The spectrum then levels off before continuing to fall with increasing wavelength. The level region extends to higher wavelengths as the solution is aged. A small peak at ~450 nm also forms. All the aging effects are the same as those in the iron-cobalt solution upon aging. Visual inspection of the iron solution after aging corroborates the color change, as the solution went from a pale yellow to a darker yellow-green. These results indicate that the color change in the iron-cobalt solution can be attributed to a change in iron species in solution over time.

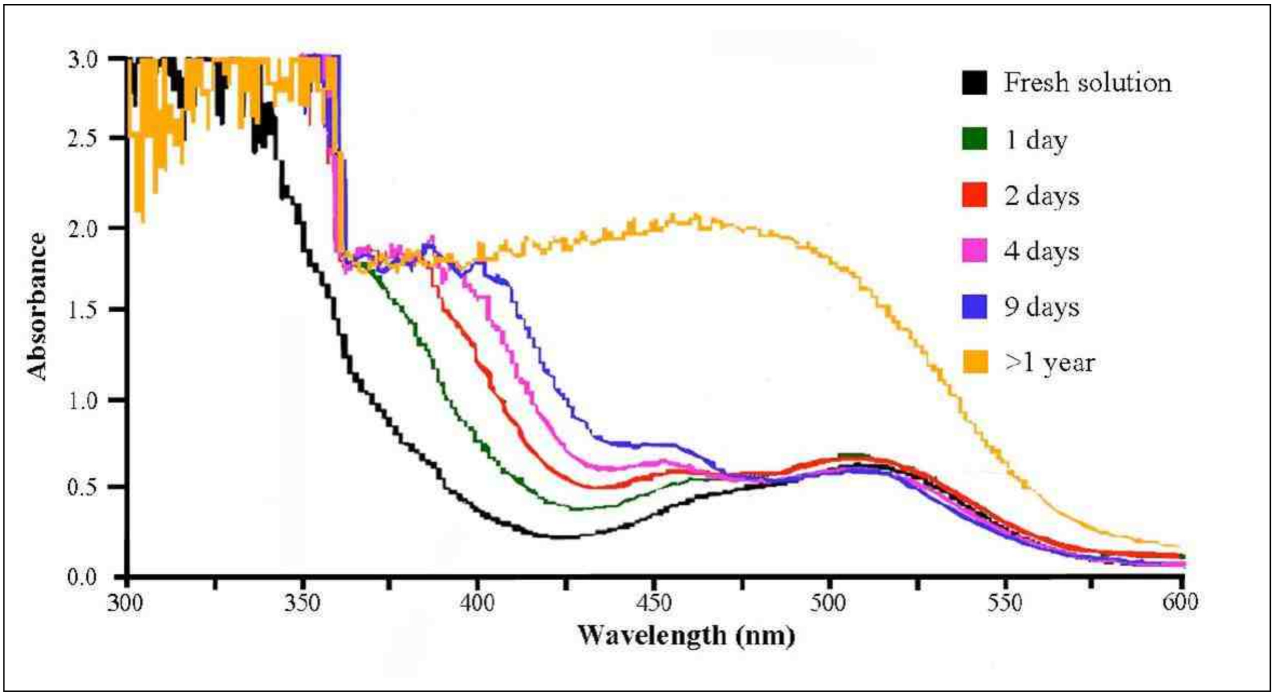

Figure 2 - UV-visible absorption spectra for iron-cobalt solution prepared with dibasic ammonium citrate: fresh solution and aged.

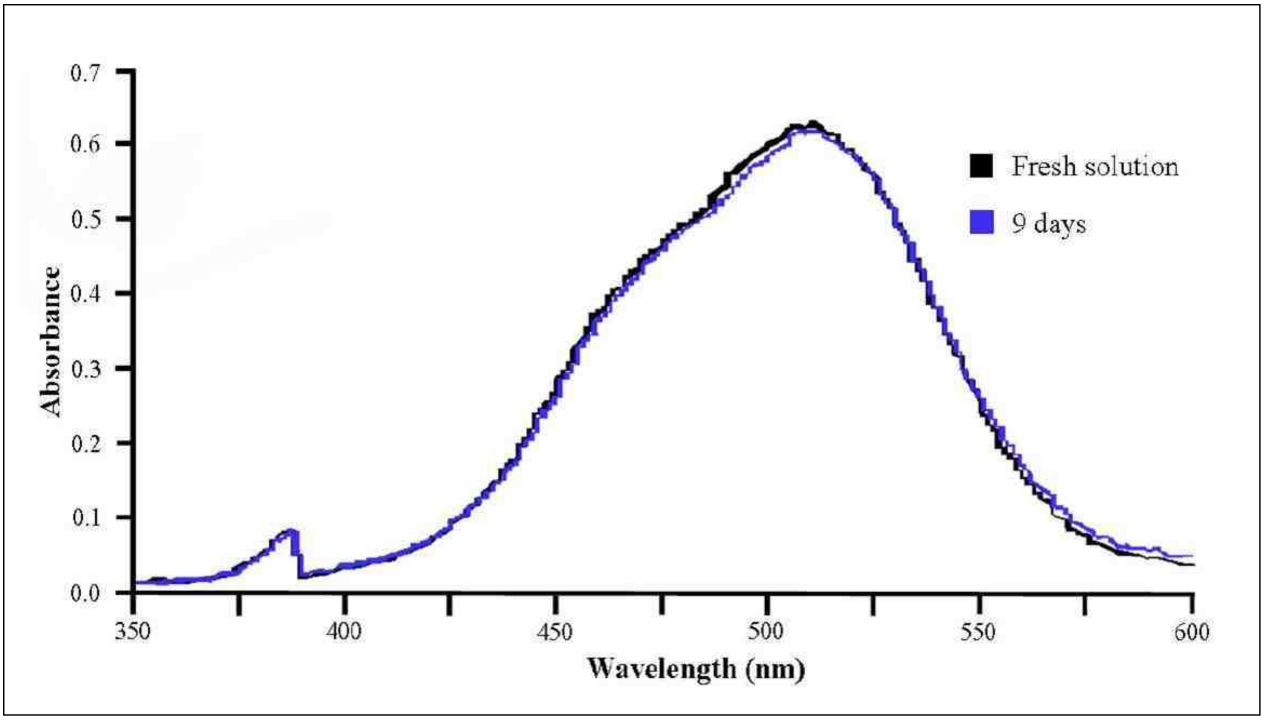

Figure 3 - UV-visible absorption spectra for solution containing only cobalt cations: fresh solution and solution aged for nine days.

Effects of dissolved oxygen on solution stability

Since the color change appears to initiate at the solution-air interface, it seems likely that the reaction is an oxidation reaction caused by dissolved oxygen. UV-visible absorption spectra for iron-cobalt solutions, which were stored in fully filled and sealed containers and not exposed to air, are shown in Fig. 5. The lack of contact between the iron-cobalt solution and air greatly limits both the extent and rate of reaction in the solution. After 29 days of storage, the solution only experienced a change comparable to a solution stored for one day when exposed to the atmosphere. The small change in the spectra in Fig. 5 is likely due to dissolved oxygen in the solution prior to storage. When an iron-cobalt solution containing Fe(III) cations was produced by replacing $FeSO_4 \cdot 7H_2O$ with $FeNH_4(SO_2)_2 \cdot 12H_2O$, the solution (natural pH = 1.9) displayed an orange hue very similar to the color that the Fe(II)-Co(II) solution showed after moderate aging.

The absorption spectra for a fresh Fe(III)-Co(II) solution at various adjusted pH values is shown in Fig. 6. The Fe(III)-Co(II) solution has absorption spectra characteristics very similar to that seen in the oxidized Fe(II)-Co(II) solu-

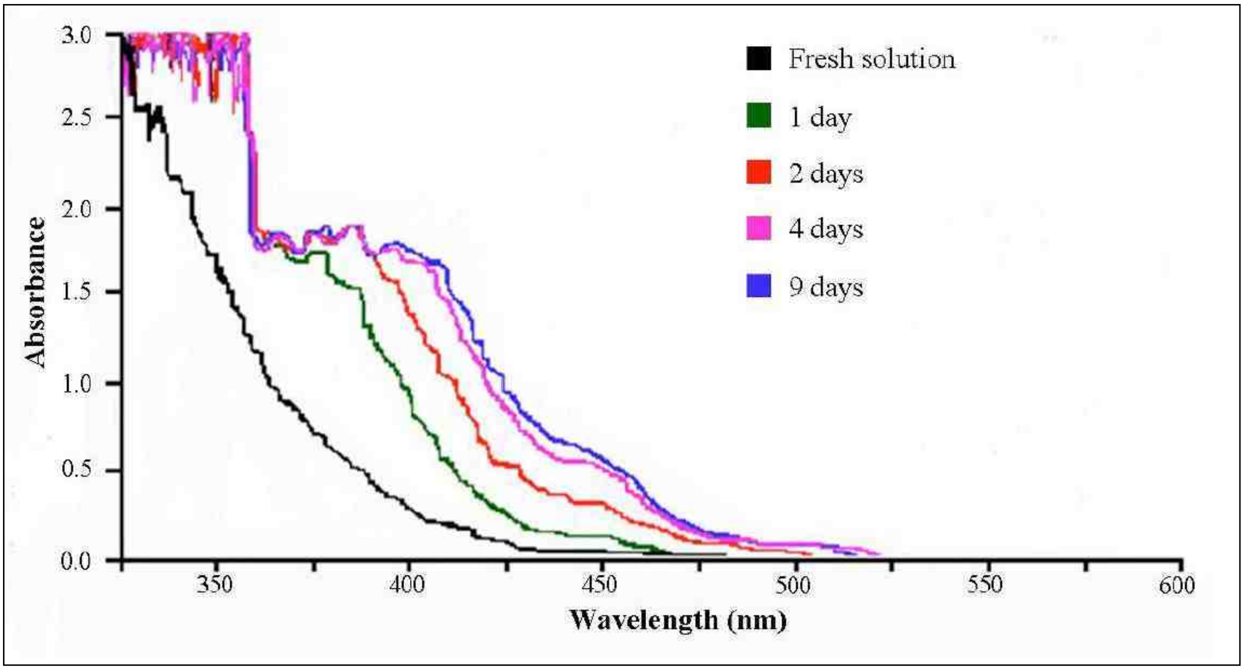

Figure 4 - UV-visible absorption spectra for solution containing only iron cations: fresh solution and aged for up to nine days.

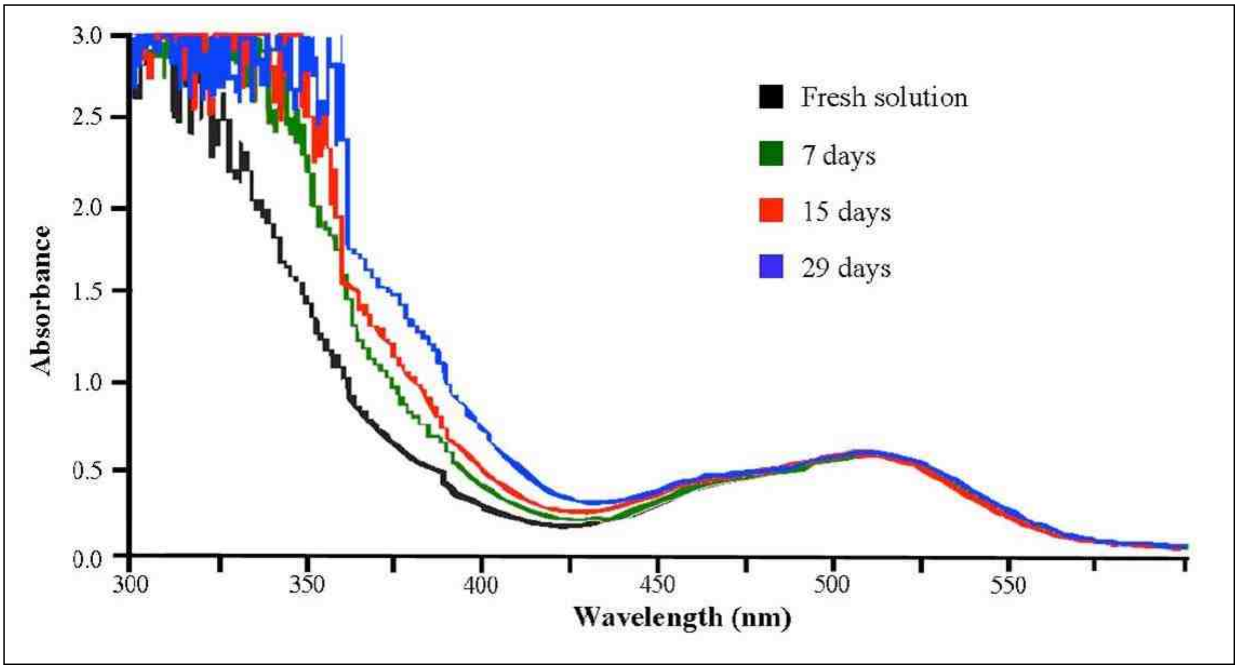

Figure 5 - UV-visible absorption spectra for iron-cobalt solution sealed from the atmosphere and aged for up to 29 days.

tion. When the pH was increased to the natural pH of the Fe(II)-Co(II) solution (~3.5), the solution showed a deep red color and precipitates became apparent. The spectra in Fig. 6 closely resemble the spectra for the Fe(II)-Co(II) solution after prolonged aging and the appearance of precipitates. These results indicate that the solution color change in the Fe(II)-Co(II) solution is likely due to a valence change in the solution from Fe(II) to Fe(III) due to the presence of dissolved oxygen. The valence change is then followed by the slow formation of an iron-based precipitate.

Effects of aging on solution pH

The pH values for Fe(II)-Co(II) solutions, exposed to and isolated from atmospheric oxygen, as a function of the age of the solution are shown in Fig. 7. The gradual decrease in pH for solutions exposed to atmospheric oxygen indicates that the formation of hydrogen ions is associated with the color change of the solution. A likely mechanism for the reaction is as follows (the standard Gibbs free energies for the reactions were calculated using values shown in Table 2):

$$2\,Fe^{+2}_{(aq)} + O_2 + 2\,H^{+}_{(aq)} = 2\,Fe^{+3}_{(aq)} + H_2O_{(l)} \qquad \Delta G^{o} = -88.7\text{ kJ} \quad (1)$$

followed by:

$$Fe^{+3}_{(aq)} + 3\,H_2O_{(l)} = Fe(OH)_{3(s)} + 3\,H^{+}_{(aq)} \qquad \Delta G^{o} = +21\text{ kJ} \quad (2)$$

and/or

$$Fe^{+3}_{(aq)} + 2\,H_2O_{(l)} = FeO(OH)_{(s)} + 3\,H^{+}_{(aq)} \qquad \Delta G^{o} = -13.2\text{ kJ} \quad (3)$$

Table 2
Gibbs standard free energies of formation for chemical species of interest

Chemical species	ΔG°_{f} (kJ/mol)*
Fe^{+2}	-78.9[9]
Fe^{+3}	-4.7[9]
O_2	0[9]
H^{+}	0[9]
H_2O	-237.1[9]
$Fe(OH)_3$	-695.0[10]
Fe_3O_4	-1015.4[9]
FeO(OH)	-492.1[11]

**Superscripts in 2nd column denote references.*

Assuming that activities can be approximated by molar concentrations and partial pressures, it can be shown from Equation (1) that at pH 3.5, when the solution is exposed to the atmosphere (the partial pressure of oxygen taken as 0.21 atm), the equilibrium concentration ratio of Fe^{+3} to Fe^{+2} is approximately 8,650. Therefore, the predominant iron ionic species are ferric ions. At the solution composition shown in Table 1, the concentration of ferric ion (Fe^{+3}) is approximately 0.048M (and that of ferrous ion (Fe^{+2}) is 5.5×10^{-6}M). It follows that the Gibbs free energy change for Equation

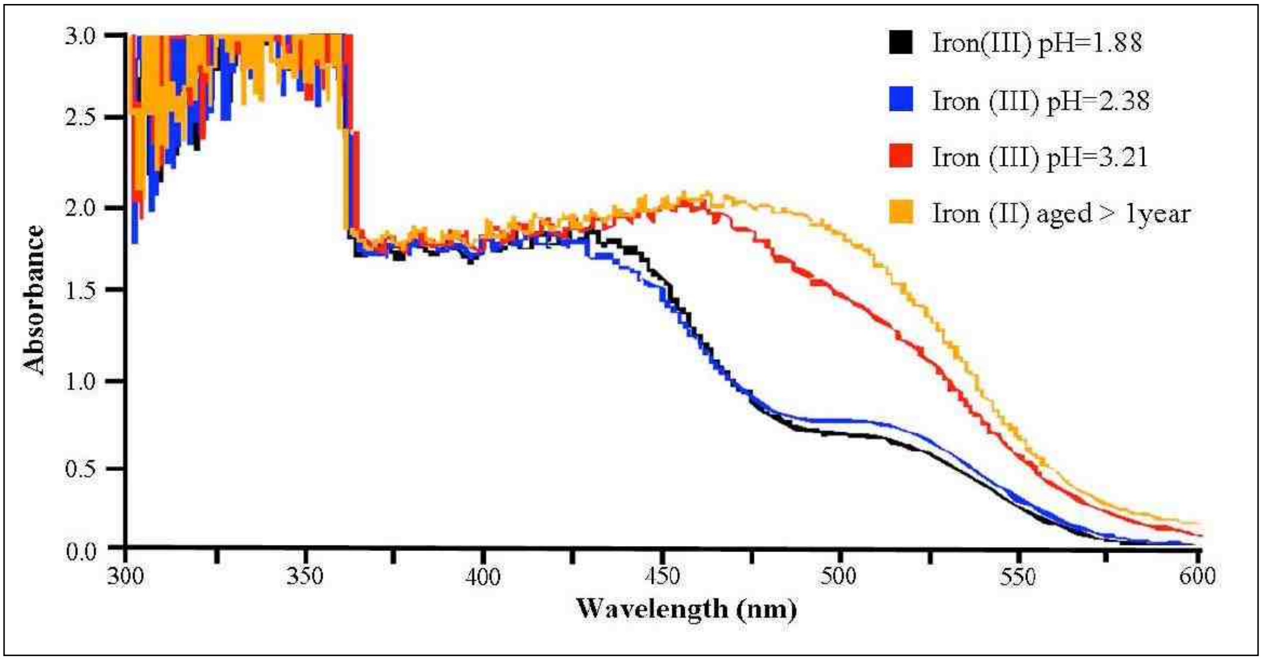

Figure 6 - UV-visible absorption spectra for Fe(III)-cobalt solution at various pH values compared with the spectrum for a heavily oxidized Fe(II)-cobalt solution (aged for more than one year).

(2) would be -31.4 kJ, and that for Equation (3) would be -65.6 kJ. Such large negative Gibbs free energy changes indicate that the formation of iron hydroxide/oxyhydroxide precipitates and a decrease in pH, as observed in this study, are indeed thermodynamically favorable under the experimental conditions.

These mechanisms are commonly observed in acidic Fe(II) solutions when adequate oxygen is available.[12,13] In addition, reactions such as these have been documented in similar iron-cobalt solutions.[4] The Gibbs free energy calculations show that at pH 3.5, the oxidation of Fe(II) to Fe(III) is energetically favorable as is the formation of $FeO(OH)_{(s)}$ and $Fe(OH)_{3(s)}$. The slow kinetics of the reactions can be attributed to the partial stabilizing effect of the dibasic ammonium citrate. The above Gibbs free energy calculations do not incorporate the influence of citrate and the formation of metal-citrate complexes in the solution. These effects were omitted due to the difficulty of obtaining thermodynamic data for the complexes. If the effects of citrate were included in the above calculations, the Gibbs free energy changes would be expected to be less negative due to the stabilizing effect on the metal ion reactants.

XPS was used to determine the identity of the precipitate. The results confirmed that the precipitate was an iron-based oxide/hydroxide. Select regions of an XPS spectrum which correspond to the iron (2p3/2 and 2p1/2) and oxygen (1s) binding energies are shown in Fig. 8. Based on the XPS spectrum, the precipitate appears to be composed of two phases: β-FeO(OH) (akaganeite)[14] and Fe_3O_4 (magnetite).[15] The relative intensities of the peaks indicate that FeO(OH) is the majority phase in the precipitate. The identification of the hydroxide phase is corroborated by the near equal intensities of the oxygen (1s) peaks in Fig. 8b, which indicates a 1:1 ratio between hydroxide and oxide groups in this phase. The presence of FeO(OH) confirms that the oxidation of Fe(II) to Fe(III) occurs in the solution [Equation (1)], followed by the reaction shown in Equation (3). There is no evidence for the formation of $Fe(OH)_3$ in the precipitate [Equation (2)]. The presence of Fe_3O_4 $((Fe^{+3})_2(Fe^{+2})O_4)$ indicates that not all the Fe(II) is oxidized to Fe(III) prior to precipitation from the solution. This phase is likely formed according to:

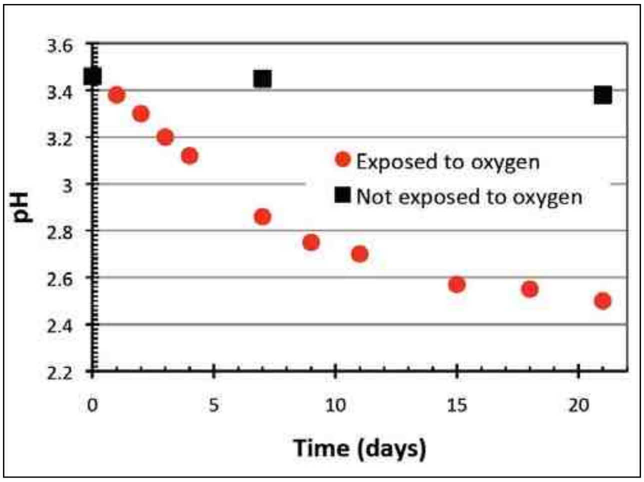

Figure 7 - The pH change in iron-cobalt solutions over time.

$$Fe^{+2}_{(aq)} + 2\ Fe^{+3}_{(aq)} + 4\ H_2O_{(l)} = Fe_3O_{4(s)} + 8\ H^+_{(aq)} \qquad \Delta G^o = +21.3\ kJ \qquad (4)$$

The positive standard Gibbs free energy change of the reaction indicates that the reaction would be favored at non-standard hydrogen ion concentrations, *i.e.*, at pH values larger than zero. The large stoichiometric value associated with the hydrogen ions, *i.e.*, 8, shows that any slight decrease in hydrogen ion concentration from 1.0M, would significantly promote the formation of Fe_3O_4 precipitates.

In fact, other researchers have shown that the electrodeposition of the Fe_3O_4 phase is typically favorable under higher pH conditions and at elevated temperatures.[16] This agrees with the Gibbs free energy calculations. Previous studies have demonstrated that the formation of iron hydroxide/oxide precipitates is associated with poor magnetic properties in iron-cobalt deposits.[4,8,17-20]

Stability of dibasic ammonium citrate stabilized solutions during use

UV-visible light absorption spectra obtained from fresh solutions after heating and/or use for electrodeposition (Fig. 9) show that both heating and the application of a potential across the cell accelerate the aging process. The decrease in solution stability at elevated temperatures is likely due to the influence of higher amounts of available ambient energy, which leads to increased rates of reaction. The potentials applied across the solution during electrodeposition likely accelerate the aging process in two ways: (1) they cause the oxidation of Fe(II) to Fe(III) at the anode and (2) cause the decomposition of water at the cathode to produce hydrogen gas and hydroxyl ions [Equation (2)].[4] The two effects appear to be cumulative, resulting in more severe aging in solutions used at elevated temperatures. The results show that even when fresh solutions are used, dibasic ammonium citrate is unable to prevent a change in valence and formation of precipitates in the solution. More precipitates likely form and can be incorporated into deposits when electrodeposition is done at elevated temperatures. This could result in lower saturation magnetization values in these films.

Summary

Ammonium citrate had previously been reported to be an effective agent for stabilizing iron-cobalt electrodeposition solutions by preventing the formation of precipitates and therefore extending the useful life of the solution. While it was confirmed that the addition of dibasic ammonium citrate significantly delayed the formation of precipitates in solution, visual examination and UV-visible light spectroscopy showed that the solutions had a measurable change in color, from a pink to an orange hue, after only one day. The color change intensified as the solution aging time was lengthened, eventually resulting in a solution with a deep red color and observable precipitates. The color change was accompanied by a decrease in solution pH. The initial color change from pink to orange resulted from the oxidation of iron ions in the solution, from Fe(II) to Fe(III), due to the presence of dissolved oxygen. After significant aging, the solution obtained a deep red color, which was attributable to the formation of precipitates in the solution. The precipitates were identified as primarily β-FeO(OH) (akaganeite) with small quantities of Fe_3O_4 (magnetite). Solution stability was shown to be further reduced by increasing the temperature and applying a voltage (electrodeposition) across the solution. These effects are cumulative and result in significant aging effects even in fresh solutions after electrodeposition.

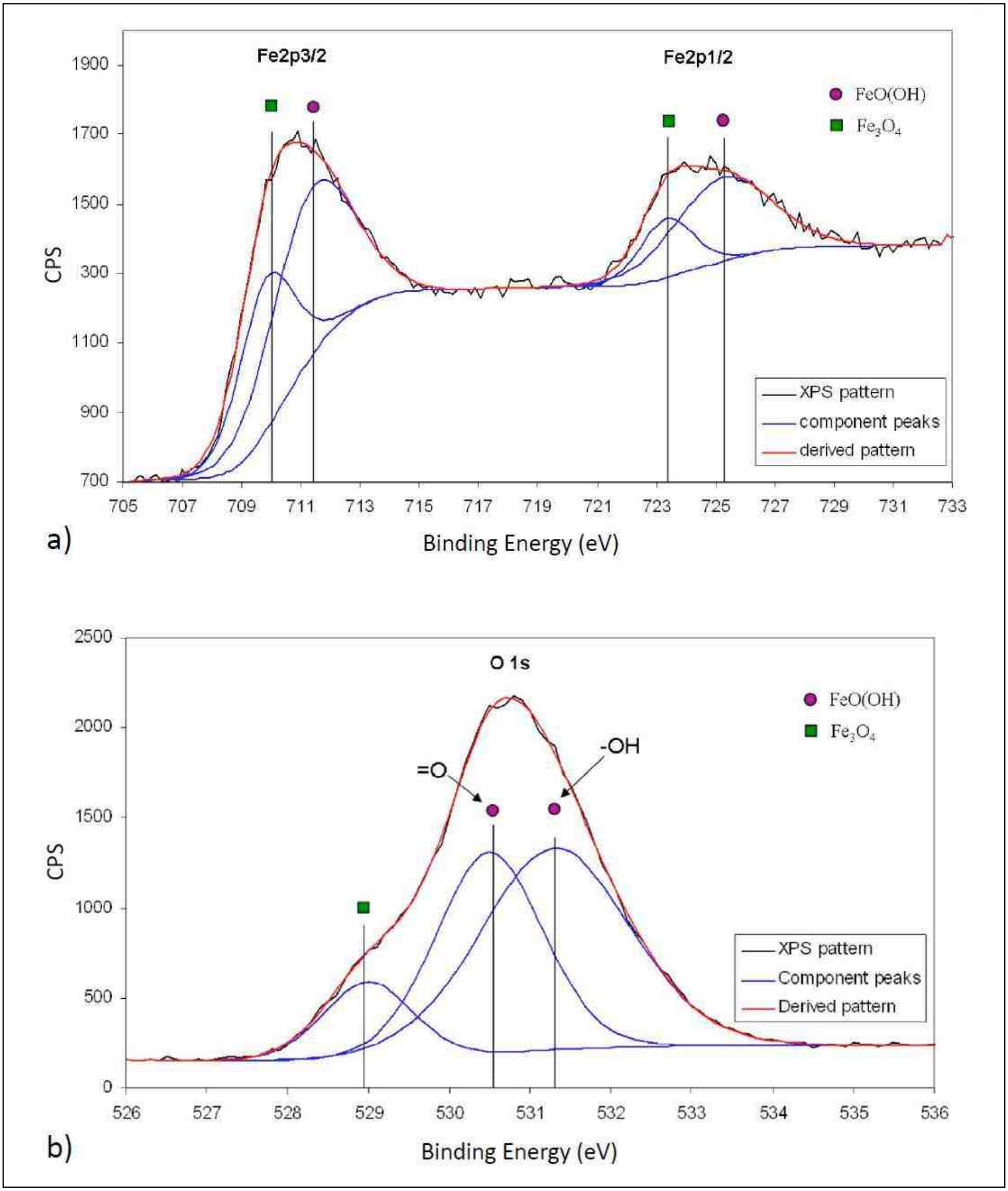

Figure 8 - XPS spectra obtained from an Fe-Co solution precipitate: (a) iron (2p3/2 and 2p1/2) peaks and (b) oxygen (1s) peaks. The peaks were deconvoluted using CASA software.

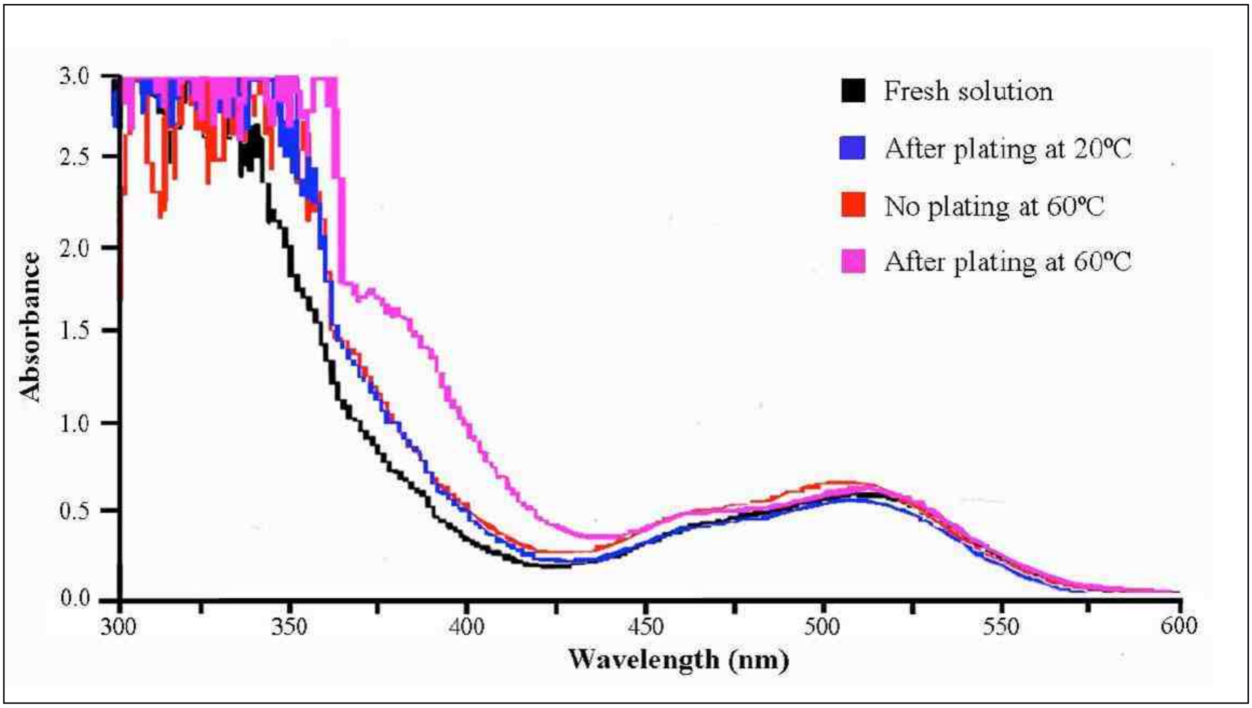

Figure 9 - UV-visible absorption spectra for fresh solutions after heating and/or after deposition of iron-cobalt thin-films.

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