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Corrosion Inhibition of a Cu-Ni Alloy in LiBr+Ethylene Glycol+H_2O Mixtures with Nitrates, Chromates and Molybdates

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A study of the corrosion inhibition of a 90(wt.%)Cu-10Ni alloy in a 55LiBr+ethylene glycol+H_2O solution by using inhibitors such as lithium chromate, lithium molybdate and lithium nitrate in a concentration of 5 ppm, have been evaluated at different temperatures (25, 50 and 80°C). Employed techniques included potentiodynamic polarization curves, linear polarization resistance and potentiostatic measurements. Results have shown that in all cases, the alloy had an active-passive behavior, but, at 25 and 50°C, the passive film properties were improved with the addition of inhibitors, whereas at 80°C the inhibitors did not have any affect them. Similarly, in general terms, the best corrosion performance at 25 and 50°C was obtained by adding $LiNO_3$, whereas at 80°C, the best inhibitor was Li_2CrO_4. However, the alloy was very susceptible to pitting corrosion in presence of both $LiNO_3$ and $LiMoO_4$, whereas this susceptibility drastically decreased with the addition of Li_2CrO_4.

Keywords: Cu-Ni alloy, inhibitors, corrosion.

1. INTRODUCTION

Absorption heat transformers are some of the most promissory elements to make an improvement of the industrial waste heat, the geothermic and solar heat which comes from higher energy levels. Lithium bromide (LiBr) heavy brines are one of the most widely used absorbents [1-3] because of its favorable thermo physical properties, high heat of hydration, high solubility of solid phases, good thermal stability, and appropriate viscosity. However, it can cause serious corrosion problems to the metallic components used in the system. Although LiBr possesses favorable thermophysical properties, it can cause serious corrosion problems on metallic components of cooling systems and heat exchangers at absorption plants such as carbon steel, stainless steel, copper alloys and titanium [4-6]. Some other disadvantages of the LiBr/water mixtures are: a) low working pressure, b) high corrosion at high temperatures, and c) tendency to crystalline at high concentrations of LiBr. An alternative way to reduce some of these disadvantages of the water/LiBr mixture is to add ethylene glycol to the system [7] because some thermo physical properties of the LiBr/water mixture, such as thermal conductivity, viscosity, maximum concentration etc.. are improved [8]. However, there are not data available concerning the corrosion problems that can be found in this system.

Copper and copper alloys are used widely in heat exchangers, steam condensers, and some other heat absorption systems because of their mechanical properties and thermal conductivity. It is widely known that the alloying of copper produces superior mechanical properties although this can present particular corrosion problems such as the selective attack of certain phases in bronzes and brasses. Corrosion inhibitors are compounds which, added to a corrosive system in some appropriated amount, can reduce considerably corrosion rates. However, there exist very few inhibitors which satisfy at the same time both technological and ecological requirements [9]. In practice, inhibitors are used for corrosion control in closed systems and as an alternative of efficiency-cost for materials use. The affectivity of some corrosion inhibitors depends upon the type of material, its properties and the corrosive environment. Chromate (CrO_4^{2-}) is a very effective passivating inhibitor at relatively high levels. It is very effective for ferrous alloys in the presence of halide ions. It can passivate metals by forming mono-atomic or polyatomic oxide film on the electrode surface. Thus, chromates are very good inhibitors to prevent pitting corrosion for stainless steels.

It is generally assumed that in acidic media, corrosion inhibitors adsorb on the metal surface which results in a structural change of the double layer and above a certain concentration ratio of non-aggressive to aggressive ions when species such as Br^- are present in the solution. The passive film formed by chromate on iron consists mainly of iron oxide and chromium oxide, which come from the oxidation of iron by chromate and the reduction of chromate [6]. However, the main disadvantage of the chromates is the chromium toxicity in the oxidation state (VI) [6].

Nitrates (NO_3^{2-}) and molybdates (MoO_4^{2-}) are inorganic, passivating inhibitors which have been used satisfactorily in many corrosive environments. For instance, molybdates have been used to prevent mild steel [10] and cold rolling steel [11] corrosion in simulated cooling water, in the zinc corrosion inhibition in acidic solutions [12], used to seal phosphate coatings on hot-dip galvanized steel [13] or on the bacterial corrosion or iron [14]. On the other hand, nitrates have been used on the corrosion inhibition of galvanized steel and aluminum[15] and zinc [16] in NaCl solutions, for the zinc corrosion inhibition in acidic solutions [14], on the pit initiation of pure aluminum in HCl solutions [17] or even used in sol-gel coatings for mild steel [18].Thus, the objective of this work is to evaluate the corrosion rate of a CU-Ni alloy, so often in heat exchanger systems, in the LiBr+ethylene glycol + water, as new absorber fluid, and evaluate the use of inorganic inhibitors such as CrO_4^{2-}, NO_3^{2-}, MoO_4^{2-} etc.. as alternative candidates for organic compounds, less toxic, cheaper, etc…

2. EXPERIMENTAL PROCEDURE

Material used in this work was a 90 (wt.%)Cu-10Ni alloy melted using an induction furnace. Cylindrical probes with 5.9 mm in diameter and an exposed area of 0.2728 cm^2 to the solution, encapsulated in resin, were used. All of them were abraded with 600 SiC emery paper, and finally rinsed with distilled water and ethanol (C_2H_5OH). Solution used was a LiBr+ethyleneglycol+H_2O mixture at 25, 50 and 80°C, in a concentration of 614 and 217 g/l for LiBr and ethylene glycol respectively, with additions of 5 ppm of either $LiNO_3$, Li_2MoO_4, or Li_2CrO_4 as corrosion inhibitors. Polarization curves were obtained by polarizing the specimens from -600 to 600 mV respect to the free corrosion potential value, E_{corr}, at a scanning rate of 60 mV/min. Corrosion current density values, I_{corr}, were calculated by using Taffel extrapolation method. A silver/silver chloride (Ag/AgCl) electrode was used as reference electrode with a Lugging capillary bridge, whereas a platinum wire was the auxiliary electrode. Once the polarization curves were performed, some potentiostatic current readings were recorded by polarizing the specimen at the pitting potential value, E_{pit}, during 3600 s. Linear polarization measurements, LPR, were carried out by polarizing the specimen from +10 to –10 mV respect to E_{corr}, at a scanning rate of 1 mV/s every 20 minutes during 10 days for 25 and 50°C, and during 24 hours for the temperature of 80°C because of solution evaporation.

3. RESULTS

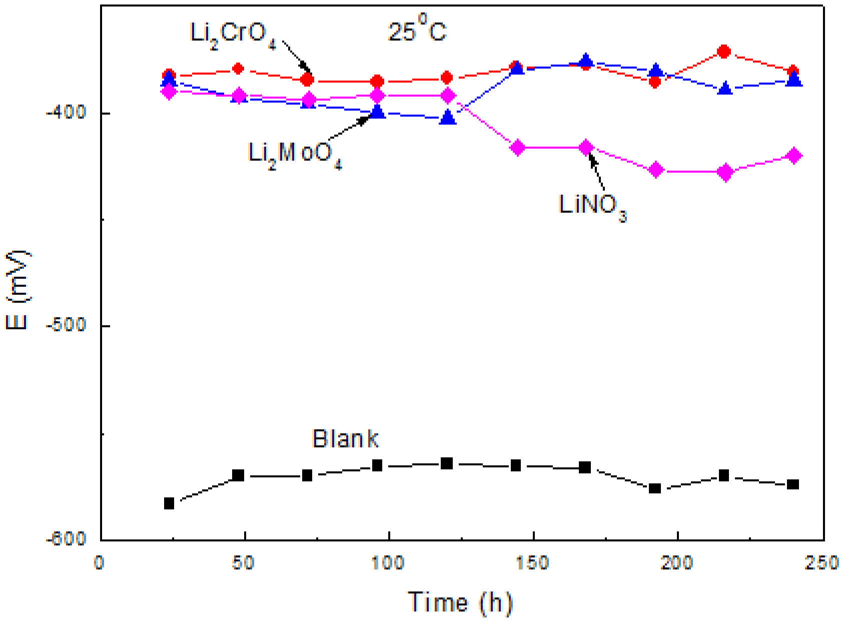

Figure 1. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the variation of the E_{corr} value with time for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 25°C.

The effect of adding 5 ppm of $LiNO_3$, Li_2MoO_4, or Li_2CrO_4 on the fluctuation of the E_{corr} value with time for the 90Cu-10Ni alloy in the LiBr+ethyleneglycol+H_2O mixture at 25°C is given in Fig. 1, where it can be seen that the most active value corresponds to the uninhibited solution, around -575 mV and remained very constant during the 240 hours of testing. As soon as the inhibitors were added, the E_{corr} value shifted towards nobler values, around -400 mV regardless of the inhibitor chemical composition. It is very well known that these inhibitors are anodic, passivating type of inhibitors, thus, the shifting towards nobler E_{corr} values when the inhibitors are added is due to the formation of a passive film formed by the inhibitors. Fig.2 shows the effect of adding 5 ppm of $LiNO_3$, Li_2MoO_4, or Li_2CrO_4 on the polarization curves of 90Cu-10Ni alloy in the LiBr+ethyleneglycol+H_2O mixture at 25°C. It can be seen that all the alloys show an active-passive behavior, with the lowest E_{corr} value for the blank solution, around -786 mV, whereas all the inhibitors made this value nobler, between -440 mV, for chromate, and -483 mV, for nitrate.

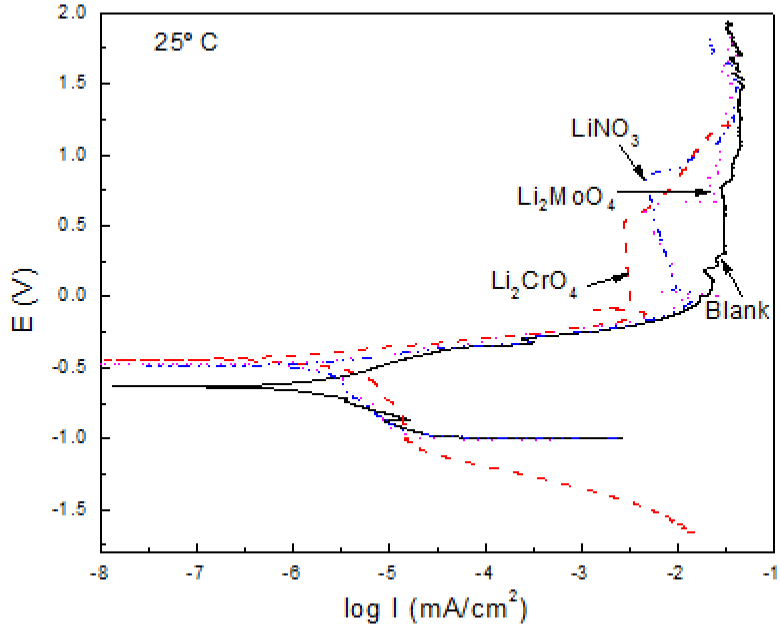

Figure 2. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the polarization curves for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 25°C.

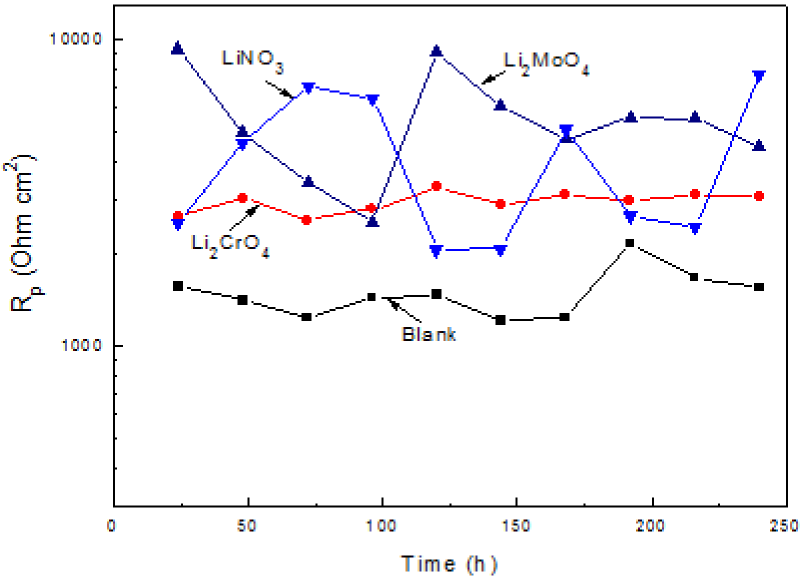

Figure 3. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the change in the R_p with time for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 25°C.

The passivation potential, E_{pass}, was lowest for nitrates, around -110 mV, whereas the noblest value was for the blank solution, close to 135 mV. The passive current density, I_{pass} was lowest for nitrates also, with a value close to 7 X 10^{-3} mA/cm^2, nearly one order of magnitude lower than that shown by the blank solution, 5 X 10^{-3} mA/cm^2 which was the highest value. The pitting potential, E_{pit}, was lowest for the blank solution, although it was not so clear, since several anodic peaks in the passive current density, but an average value of 284 mV was taken. The highest E_{pit} value was obtained for the solution with nitrates, 617 mV.

Thus, at short times, according to the polarization curves, the best inhibitor seemed to be nitrates. However, a better evaluation of inhibitors is longer times testing, and Fig. 3. which shows the effect of the different inhibitors on the change in the polarization resistance, $R_{p,}$ with time at 25°C during ten days. It can be seen the lowest R_p value, and thus, the highest corrosion rate, was for the uninhibited, blank solution, followed by the solution containing chromates, with an R_p value almost twice bigger than that for the blank solution. The solutions containing either nitrates or molybdates showed the highest R_p values, up to eight times higher than the value obtained for the uninhibited solution, although their values showed some instabilities with time, indicating that their formed protective films can be detached from the alloy surface, allowing the electrolyte to corrode the metal. Inhibition efficiencies [*IE(%)]* can be determined according to the following equation:

$$E(\%) = \frac{R_{p,i} - R_{p,b}}{R_{p,i}} \text{ X } 100 \qquad [1]$$

where $R_{p,b}$ is the linear polarization resistance without inhibitor and $R_{p,i}$ is the linear polarization resistance with inhibitor. Results for $LiNO_3$ are shown in Fig. 4.

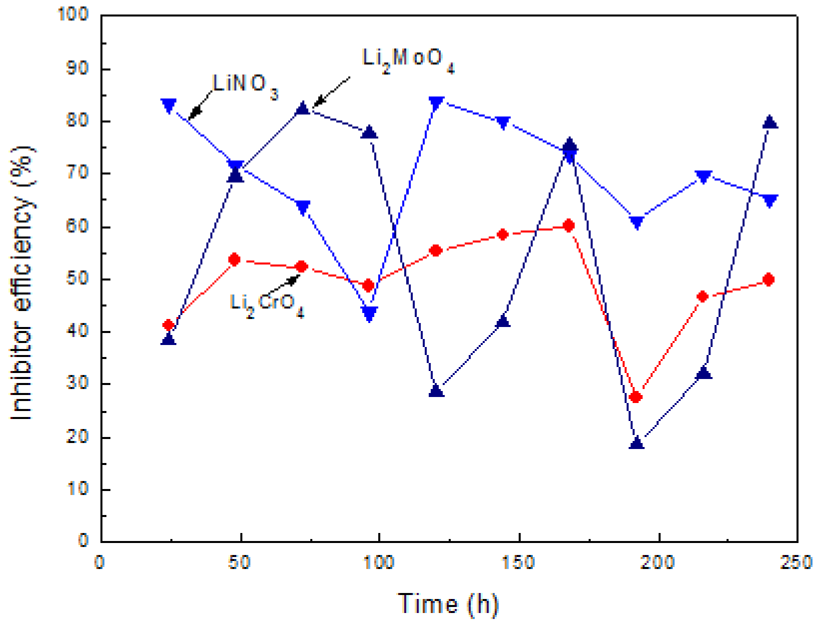

Figure 4. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the change in the inhibitor efficiency with time for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 25°C.

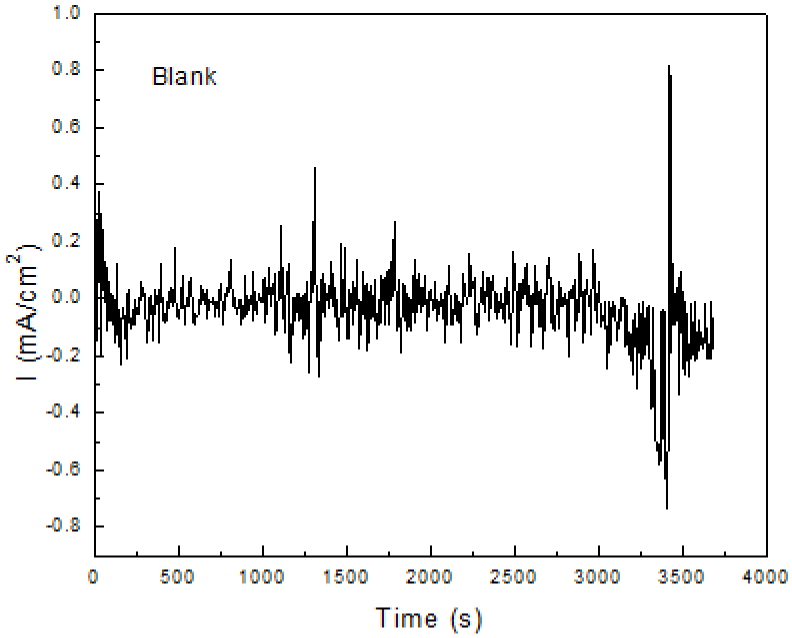

Figure 5. Change in the current density with time for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 25°C hold at + 280 mV.

This figure shows that the best inhibitor efficiency was obtained with the addition of either $LiNO_3$ or Li_2MoO_4, around 80% whereas the lowest efficiency was obtained with the addition of Li_2CrO_4, lower than 60%.

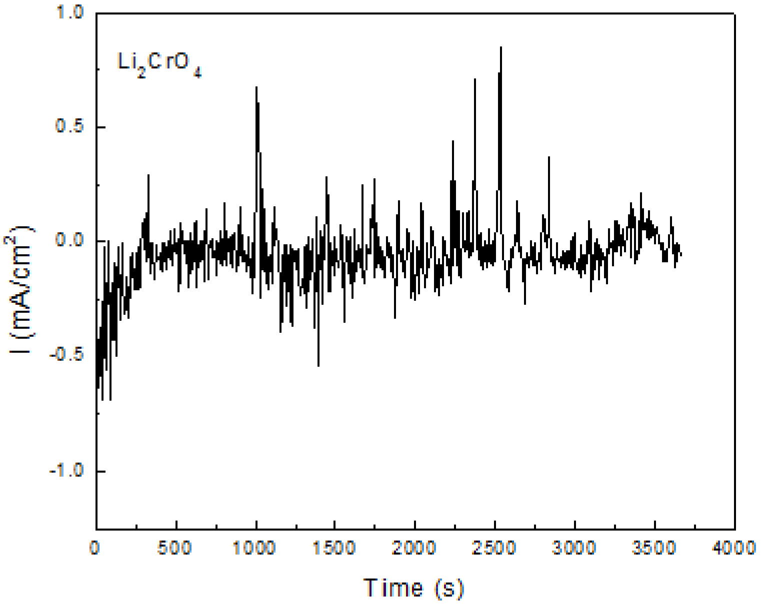

Figure 6. Change in the current density with time for 90Cu-10Ni alloy in the chromate-containing solution at 25°C hold at + 537 mV.

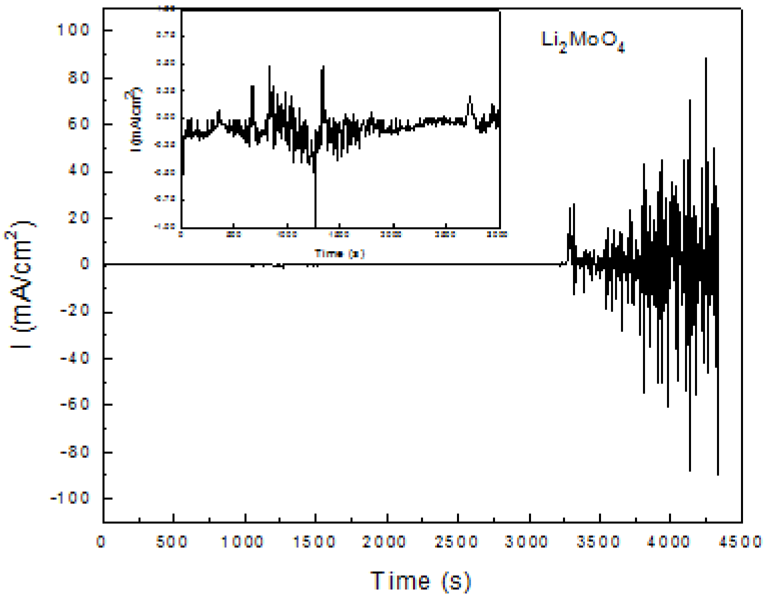

Figure 7. Change in the current density with time for 90Cu-10Ni alloy in the molybdate-containing solution at 25°C hold at + 617 mV.

It can be seen in Fig. 3 that the R_p values when the inhibitors are added showed some fluctuations with time, thus, in order to evaluate the inhibitor formed film stability, the alloy was hold at the pitting potential values during between 3600 and 4000 s and the current registered. Fig. 5 shows the current for the blank solution when the alloys was polarized at 280 mV. This figure shows that the current has some fluctuations with low intensity and high frequency, typical of a metal undergoing passivation just as shown on Fig. 2. For the alloy in presence of chromates hold at 537 mV, Fig. 6, the current shows fluctuations with higher intensity but lower frequency than that exhibited by the blank solution. The anodic increase in the current value indicates a rupture of the passive film, whereas the slow decay in the current value indicates the rebuilding of the passive film. Thus, these transients indicate passive film rupture-repassivation events.

This kind of behavior is typical of a passivated material, but, in some points, the passive layer is broken, and a localized form of corrosion is nucleated, what is called metastable pit, but, as soon as the film is repassivated, the pit stops growing. For the alloy in presence of molybdates and hold at 617 mV, Fig. 7, the current fluctuations starts in a low magnitude, but this value starts to increase in intensity and frequency. The intensity of the current fluctuations is much higher than that found either in the blank solution or in the solution containing chromates, indicating that the pits are not any longer metastable, but, instead, they are propagating pits. The anodic increase in the current represents the rupture of the passive film, whereas the cathodic current represents the repassivation of this film. Finally, in the solution containing nitrates, Fig. 8, the current fluctuations were lower in magnitude than those shown on presence of molybdates, but still much higher than that found in the blank solution or in presence of chromates. After some time, however, the intensity of these fluctuations decreased in intensity, but not in frequency, indicating metaestable, no-propagating pits.

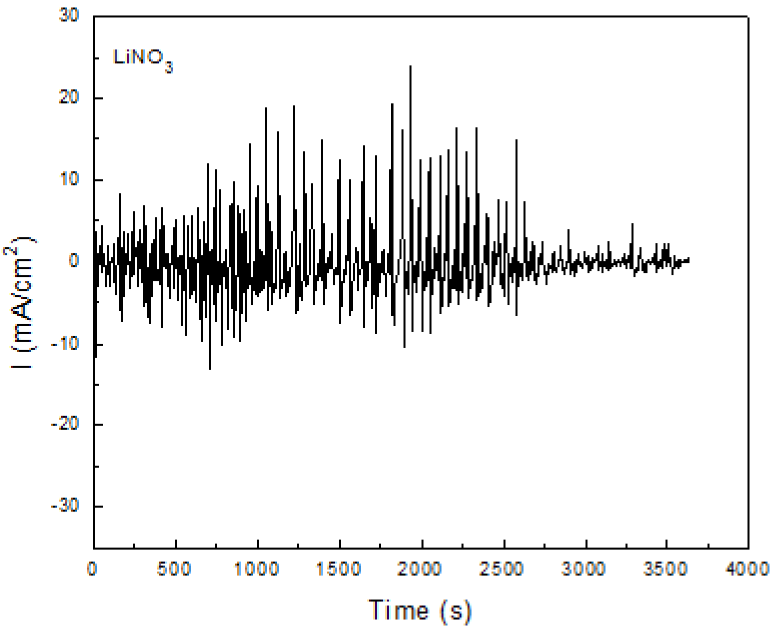

Figure 8. Change in the current density with time for 90Cu-10Ni alloy in the nitrate-containing solution at 25°C hold at + 850 mV.

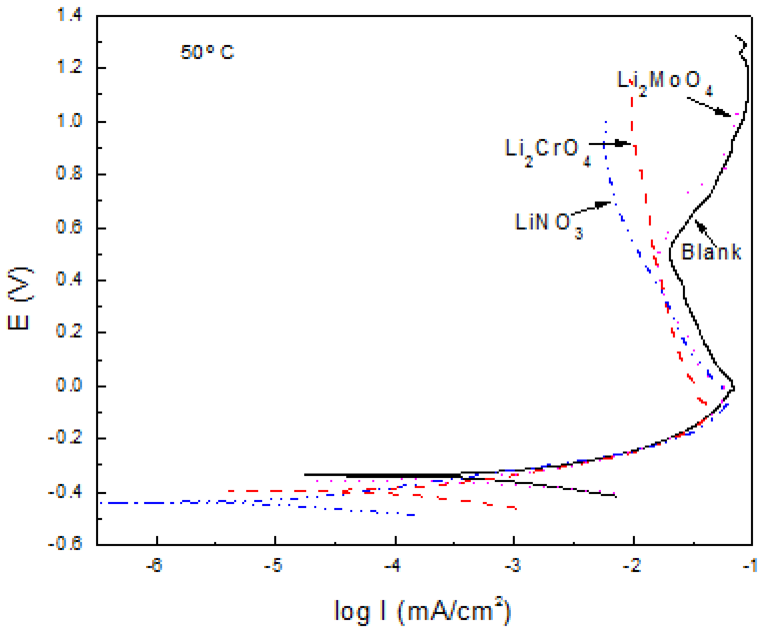

Figure 9. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the polarization curves for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 50°C.

Polarization curves for inhibited and uninhibited solution at 50°C are shown on Fig. 9. It can be seen that the E_{corr} value for the blank solution has increased towards nobler values, close to -330 mV, whereas the corrosion current density has increased, respect to the data at 25°C, by two orders of magnitude. The passive current density, however, remained more or less constant as compared with the value obtained at 25°C. For inhibited solutions, the E_{corr} values increased slightly towards nobler values and so the I_{pass} values did. This time it was not possible to find the E_{pit} value for solutions containing either chromates or nitrates in the range of potentials tested, but the blank or molybdates containing solution had values of 526 and 516 mV respectively.

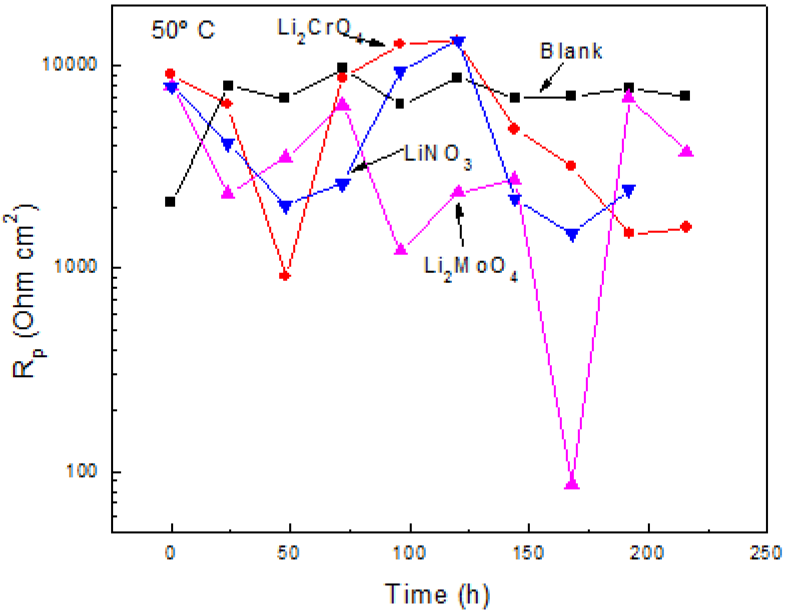

Figure 10. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the change in the R_p with time for the 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 50°C.

This time, the lowest I_{pass} obtained value was for the nitrates-containing solution, whereas the highest value was for the uninhibited, blank solution, although the difference was marginal. At longer times, Fig. 10, during most of the testing time, the highest R_p values were obtained for the blank solution, whereas the lowest was for the solution containing molybdates, although in some cases, the R_p for the chromates-containing solution was similar to those obtained for the uninhibited solution. Therefore, the inhibitor efficiency values were negatives, Fig. 11, indicating a degradation of the inhibitors as the temperature increases. Compared with the values obtained at 25°C, all the inhibited solutions at 50°C showed similar R_p values, except the blank solution, where an increase in the temperature brought and increase in the R_p values, thus, a decrease in the corrosion rate.

At 80°C, all the polarization curves, regardless the presence of inhibitors, showed an active-passive behavior with very similar features, with an E_{corr} value close to -470 mV and passive current density values between 1-5 X 10^{-5} mA/cm^2, Fig. 12, much lower than those values found at both 25 and 50°C. The lowest I_{pass} value was obtained with chromates, whereas the highest was obtained with molybdates. No pitting value was found for the range of potentials tested. The effect of the different inhibitors on the change of the R_p value with time is shown on Fig. 13, where it can be seen that the lowest R_p value, and thus the highest corrosion rate, was obtained with nitrates. For times shorter than ten hours, the highest R_p value, the lowest corrosion rate, was obtained by adding chromates, but, after this time, the R_p value obtained with this inhibitor was similar to those obtained in both the blank solution and by adding 5 ppm of molybdates. Thus, whereas at 25 and 50°C lithium nitrates seemed to be the inhibitor which decreased the most the corrosion rate, at 80°C lithium chromate seemed to be the best inhibitor although this difference was marginal, which was more evident when the inhibitor efficiency values are calculated, Fig, 14, where it can be seen thatd uring the first 10 hours, the best efficiency was obtained with Li_2CrO_4, less than 60%, whereas the worst performance was obtained with $LiNO_3$.

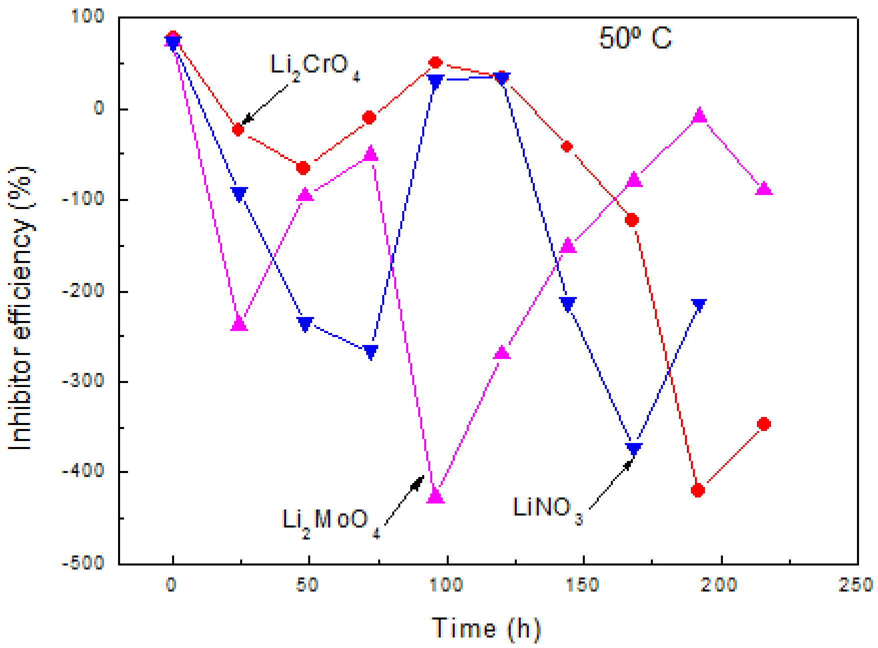

Figure 11. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the change in the inhibitor efficiency value with time for the 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 50°C.

Anodic inhibitors such as chromates, nitrates and molybdates, are, in most cases, species that form insoluble salts with the ions of the corroding metal, thus rendering the surface passive. Therefore, their effectiveness will depend upon the metal and their chemical composition. For chromates, thick corrosion inhibiting layers are usually assumed to form on the metal surface via precipitation of insoluble products from the solution. For instance, the passive film on iron by chromates consists mainly of iron oxide and chromium oxide which come from the oxidation of iron by chromate and the reduction of chromate. Possible process for chromates is the reduction or decomposition of the inhibitor on the metal surface, followed by precipitation. Chromates are reduced from Cr^{6+} to Cr^{3+} (as Cr_2O_3) during film formation [19]. The passive film formed on iron by chromate mainly consists of iron oxide and chromium oxide which come from the oxidation of iron by chromates and the reduction of chromate. Possible reduction reaction of CrO^{2-}_4 occurring on the electrode surface is as follows [20]:

$$2\ CrO^{2-}_4 + 10H^+ + 6e^- \rightarrow Cr_2O_3 + 5H_2O \qquad (4)$$

The effect of inhibitors may be explained on the basis of competitive adsorption between inorganic ions (NO_3^{1-}, CrO_4^{2-} etc,) and aggressive Br^{1-}ions, on the passive electrode surface and thus retards their corresponding destructive action.

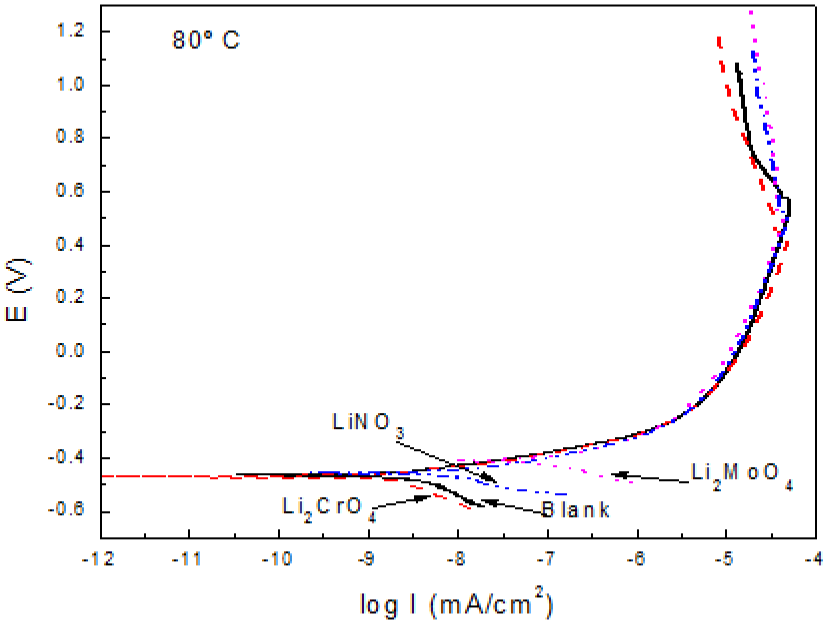

Figure 12. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the polarization curves for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 80°C.

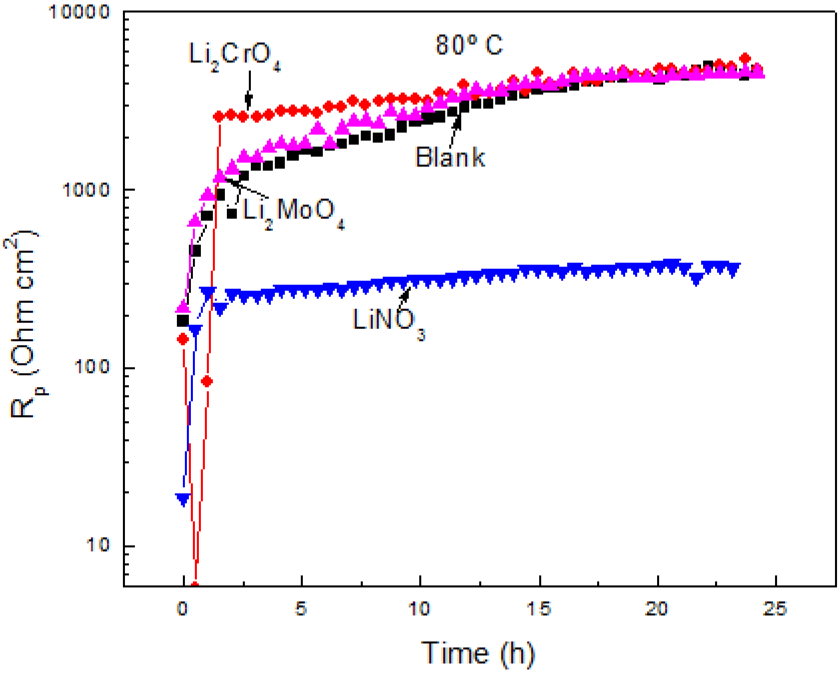

Figure 13. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the change in the R_p with time for 90Cu-10Ni alloy in 55LiBr+ethylene glycol+H_2O at 80°C.

The inhibitive anions may be incorporated into the passive layer on the metal surface forming an improved stability against aggressive ions. Specifically, the competitive adsorption of the CrO^{2-}_4 rather than the aggressive anion Br^- means that the CrO^{2-}_4 anion can displace the adsorbed Br^- ions. In the case of reduction of the Cr^{6+} species, the probable reduction, Cr^{3+}, probably deposited initially onto the bare metal, and subsequently into the growing Cr_2O_3 film or as separate phase nuclei. In a similar way, it has been shown by Virtamen [21] and by Bidawy [22] that for iron (Fe) in presence of halogens such as Cl^-, Br^-, etc.. molybdates react with Fe to form sparingly soluble $FeMoO_4$ in the precipitate within the pit, whereas in absence of the halogens, only compounds such as Fe-Cl were found.

Copper or nickel could act in a similar way. With the incorporation of molybdates into the passive film, the Cu- or Ni-molybdate layer may act as a precursor film for repasivation of the pits, by partially blocking the active sites. Further, either molybdates, nitrates or chromates replaced aggressive halogens in the pit environment. However, they did not exclude the increased pitting resistance by molybdates by other mechanism such as competitive absorption with Br^- or by modifying the passive film.

As stated above, observed transients in the current fluctuations can be associated to instabilities in the formed film by the inhibitors, but also to the incorporation of ions such as Cr^{3+} into the growing film. On the contrary, reduction of nitrate or molybdate is not expected to be involved in a similar way. The reduction products are either gaseous (as N_2, NH_3, NO, etc…) or highly soluble ions (eg. NH^+_4 or NO_2^-) which could hardly affect the properties of the growing film. Different inhibitors have a different way to be adsorbed on the substrate to form the protective film although the final result is the same, i.e. to reduce the anodic current density. Our results show this, in a similar way, indicating that one of the inhibitors, Li_2CrO_4, reduce the current fluctuations whereas $LiNO_3$ and Li_2MoO_4 did not, at least with 5 ppm

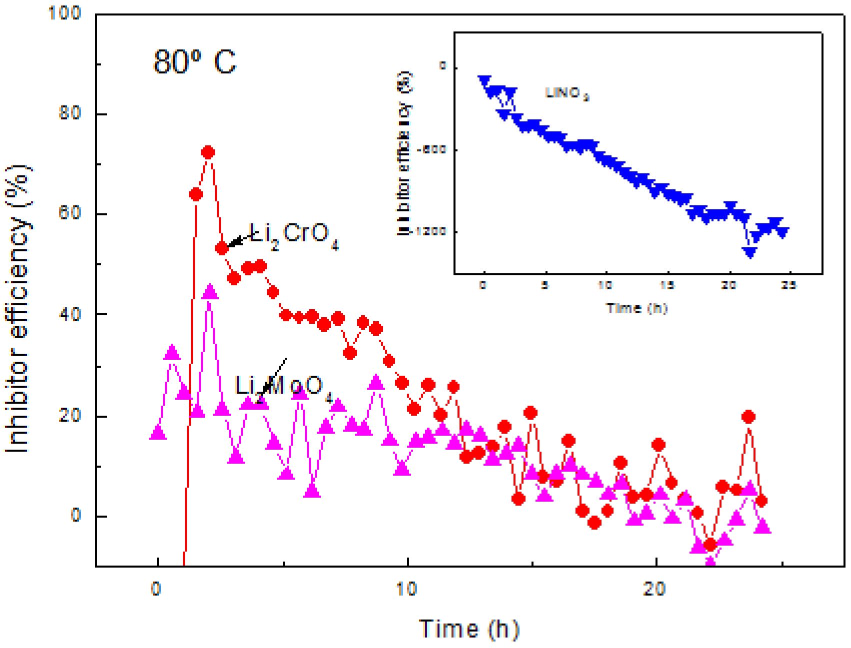

Figure 14. Effect of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the change in inhibitor efficiency value with time for 70Cu-30Ni alloy in 55LiBr+ethylene glycol+H_2O at 80°C.

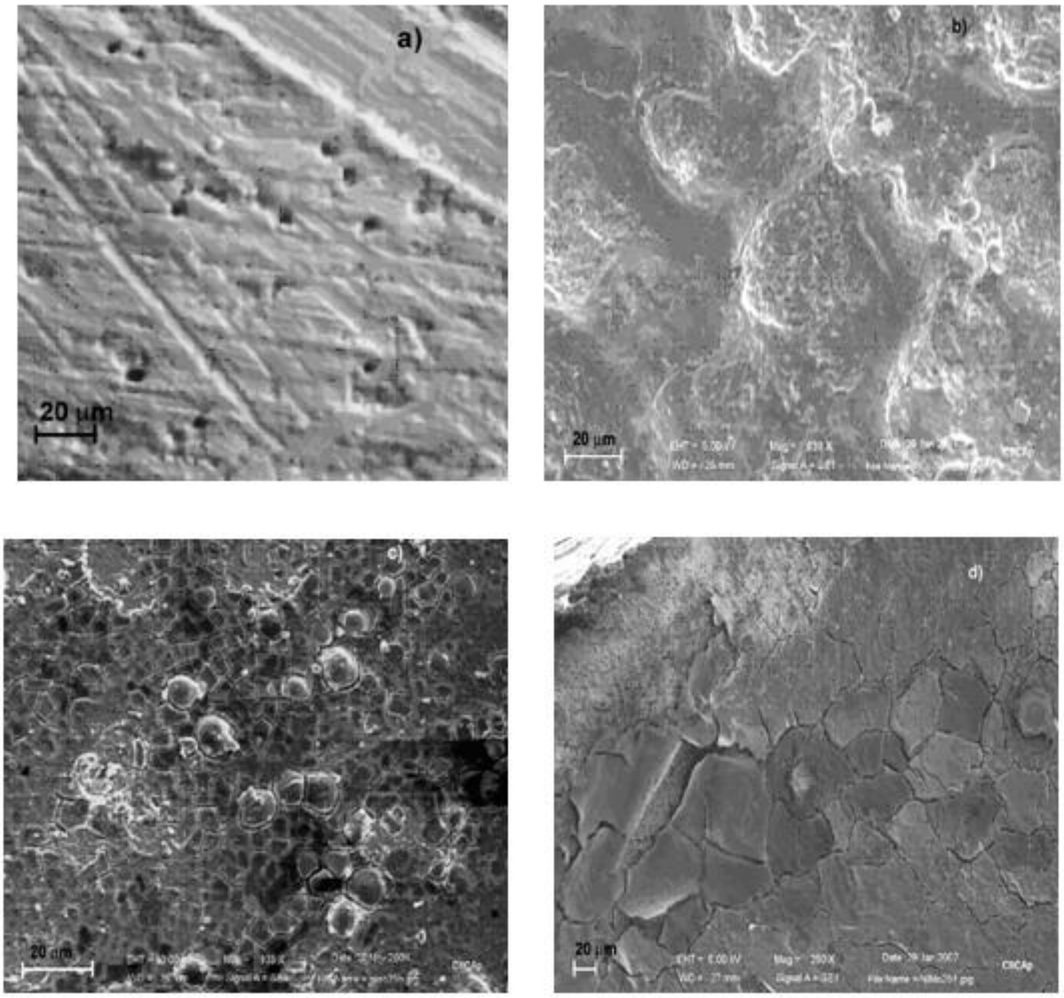

Figure 15. Micrographs of the corroded 70Cu-30Ni alloy in 55LiBr+ethylene glycol+H_2O at 25°C in a) absence of inhibitor, b) 5 ppm of $LiNO_3$, c) Li_2MoO_4, and c) Li_2CrO_4.

The corrosion resistance of a passive film is often related to its susceptibility towards local breakdown and initiation of pits. It has been demonstrated that the growth of corrosion pits occurs in two consecutive stages characterized by a metastable growth in the early period, followed by stable growth [19]. Metastable pits cause no great damage to the material since their diameter is typically of the order of a few micrometers, however, the early development of stable pits is identical to that of metastable pits [23] and the probability of stable pitting is directly linked to the occurrence and intensity of metastable pitting. Thus, in absence of inhibitors, the probability of stable pitting is higher than that when there is inhibitor present., since the number and amplitude of transients was higher in the former case than in the later. This is obvious from Figs. 3-6, where it can be seen that the probability for pitting to occur is higher at 5 ppm of lithium molybdite or lithium nitrate, than that for lithium chromate. This is common with anodic type of inhibitors: when they are used in concentrations which do not cover the entire substrate, there are some uncovered sites through which aggressive ions such as Br^- can attack the metal surface. Once a critical concentration has been reached in such a way that the whole metal surface is covered by the inhibitor, the number of active sites is lowered and, thus, the probability for localised type of attack is decreased, increasing the pitting potential value (Figs.2, 10 and 13) and lowering the frequency of the noise resistance transients (Figs. 5-8). It seems that 5 ppm of lithium chromate to inhibit pitting corrosion to occur but not for lithium molybdates or lithium nitrates.

4. CONCLUSIONS

A study on the effect of 5 ppm of $LiNO_3$, $LiMoO_4$ and Li_2CrO_4 on the corrosion performance of a 90Cu-10Ni alloy in the 55LiBr+ethylene glycol+H_2O mixture has been carried out 25, 50 and 80°C. Results have shown that in all cases, the alloy had an active-passive behavior, but, at 25 and 50°C, the passive film properties were improved with the addition of inhibitors, whereas at 80°C the inhibitors did not have any affect them. Similarly, in general terms, the best corrosion performance at 25 and 50°C was obtained by adding 5 ppm of $LiNO_3$, whereas at 80°C, the best performance was obtained with the addition of Li_2CrO_4. However, the alloy was very susceptible to pitting corrosion in presence of both $LiNO_3$ and $LiMoO_4$, but this susceptibility drastically decreased with the addition of Li_2CrO_4.

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