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Protection against corrosion in marine environments of AA5083 Al–Mg alloy by lanthanide chlorides

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Abstract

The addition of small concentrations of lanthanide chlorides to 3.5% NaCl aerated aqueous solutions inhibits uniform and pitting corrosion processes of AA5083 Al–Mg alloy. Full immersion tests combined with different electrochemical techniques have been used in order to determine the protection degree and the inhibition character supplied by the rare earth salts. Additional Scanning Electron Microscopy and Energy Dispersive Spectroscopy data have allowed us to establish some features of the inhibition mechanism.

Keywords: Aluminium alloys; Uniform corrosion; Pitting corrosion; Inhibitors; Lanthanide chlorides

1. Introduction

In recent years, lanthanide compounds have been successfully introduced to provide corrosion protection of different metallic materials such as mild and stainless steels [1–5], zinc [6] or aluminium alloys [7–12]. In these applications, lanthanide compounds are used as environmental-friendly alternatives to classical procedures, e.g. chromate based corrosion inhibitors [13,14]. Thus, lanthanide salts have been tested to prepare conversion coatings on aluminium alloys [9,15]. Research efforts have focused on the study of Al–Zn and Al–Cu alloys, usually employed in the aeronautical industry, however there are no reports about their application to Al–Mg alloys, specifically developed for marine environments [14].

The present work reports on the results obtained in the study of lanthanum, cerium and samarium chlorides, in the ppm range, as inhibitors of the Al–Mg alloy AA5083 corrosion process in aerated 3.5% sodium chloride solutions at room temperature. Special attention has been paid to the influence of the lanthanide on the pitting corrosion phenomena of this alloy.

2. Experimental

The experiments were performed using 30×25×4 mm sheets of AA5083 (Al–Mg) wrought alloy in O-temper state. The chemical composition of this alloy, in weight percent, is shown in Table 1. Prior to the corrosion tests, the surface of the samples were wet polished with silicon carbide from 220 to 500 grits, degreased with acetone and, finally, rinsed with distilled water.

Corrosion tests were carried out in oxygen saturated 3.5% NaCl aqueous solutions, at room temperature. Lanthanum, cerium and samarium chlorides were added in concentrations ranging from 100 to 1000 ppm in lanthanide cations.

Full immersion tests were performed in accordance with the ASTM-G31 standard. Exposure times between 1 and 30 days were used. Corrosion rates were determined by measuring the weight loss of the tested samples. For this purpose corrosion products were removed following the ASTM-G1 standard. After these immersion essays, microstructural features of the exposed samples were analysed in a JEOL 820 SM scanning microscope equipped with an AN-10000 LINK EDS spectrometer.

Linear polarisation techniques have been used to evaluate the degree of protection against uniform corrosion supplied by the lanthanide inhibitors, as well as to obtain information about the mechanism of the inhibition process. On the other hand, pitting corrosion inhibition degree has been evaluated in terms of both nucleation of pits and

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Table 1
AA5083 alloy nominal composition (%)

Mg	4.0–4.9
Mn	0.4–1.0
Si	0.4–0.7
Fe	0.4
Ti	0.15
Cu	0.1
Cr	<0.25
Al	The rest

upgrowth of pre-existing pits, using cyclic polarisation tests. The polarisation rate was 10 mV min^{-1} for both techniques. These electrochemical data were obtained in a EG&G Flat Cell attachment connected to a VersaStat model EG&G Potentiostat. M352 Corrosion Software of Parc Instruments was used for data processing, electrochemical parameter evaluation and potentiostat control.

3. Results and discussion

Fig. 1 plots weight loss vs. time curves of samples immersed in aerated 3.5% NaCl solutions both without inhibitor and with a 500 ppm addition of lanthanide salts. Clear differences can be noted in this figure between the samples exposed to solutions containing $LnCl_3$ and those immersed in the bare NaCl solution. Thus, the average slope of the trace of the latter is about three times that observed in the solutions containing $LnCl_3$. Otherwise, the three lanthanide salts show quite similar plots for the whole exposure time spanned in the immersion tests. As the corrosion rate depends directly on weight loss, the addition of lanthanide salts results in a significant decrease of this parameter. Therefore, $LaCl_3$, $CeCl_3$ and $SmCl_3$ can be considered as efficient inhibitors of AA5083 uniform corrosion in NaCl solutions. These results are in agreement with those previously reported in [9,10] for other aluminium alloys.

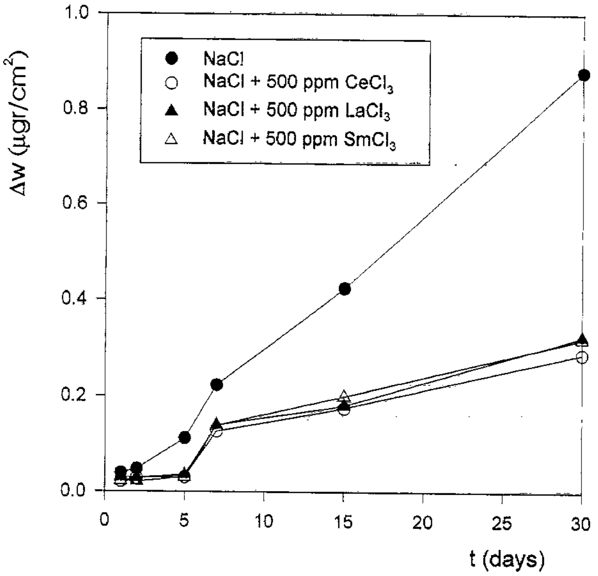

Fig. 1. Weight loss–time curves of full immersed samples of AA5083 in 3.5% NaCl aerated solutions. A decrease in weight loss by addition $LnCl_3$ can be observed.

The nature of the inhibition process has been established on the basis of linear polarisation measurements, Fig. 2. Thus, changes observed in the polarisation curves after addition of the inhibitors are usually used as criteria to classify inhibitors as cathodic, anodic or mixed [16]. In our case, the modifications caused by the addition of $LnCl_3$ to the NaCl solution are a negative shift of the corrosion potential (E_{corr}) and a leftward displacement in the cathodic branch of the curves. According to [16] these are the typical features of cathodic inhibitors, this being in agreement with the results obtained for other aluminium alloys [9,10]. The maximum displacement has been observed after an addition of 500 ppm, Fig. 3. Higher inhibitor concentrations lead to a decrease in the inhibition power, the effect being associated with the corroding power of chloride ions stemming from the concentration level existing in the 1000 ppm $LnCl_3$ solutions [5,10].

Scanning Electron Microscopy (SEM) and Energy Dis-

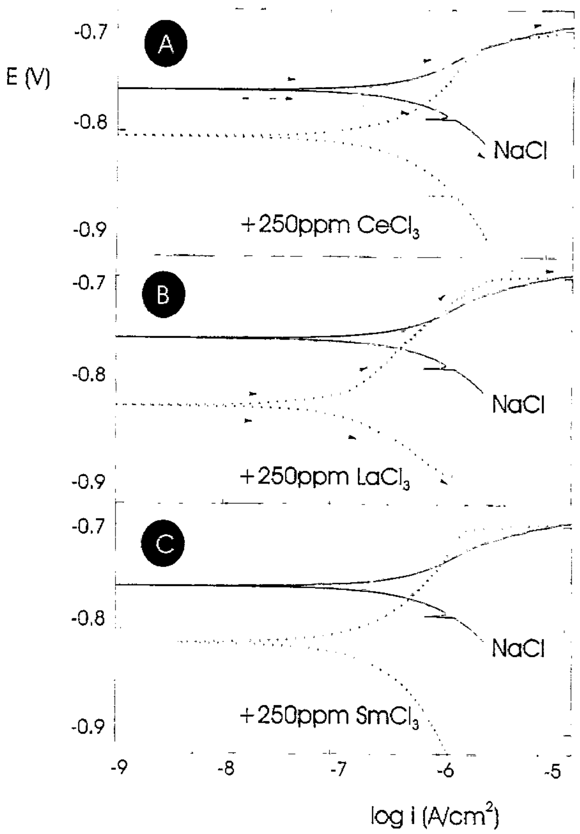

Fig. 2. Linear polarisation curves for AA5083 in bare NaCl solution and with 250 ppm additions of (A) $CeCl_3$, (B) $LaCl_3$ and (C) $SmCl_3$. Note the shifts in the corrosion potential towards active values and also the leftward displacements of the cathodic branches. Both effects result in lower values of i_{corr} and, therefore, of corrosion rate.

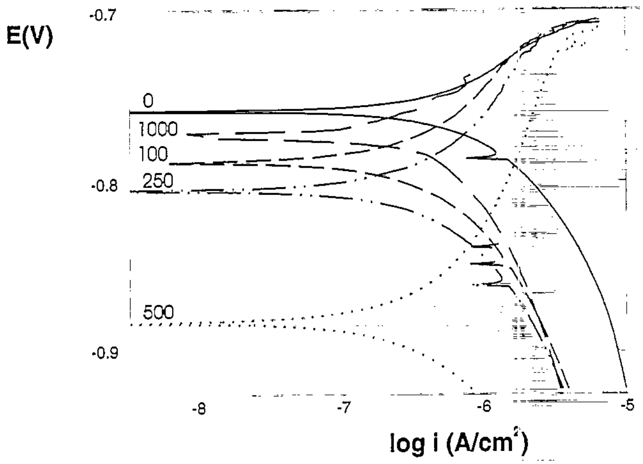

Fig. 3. Evolution of linear polarization curve of AA5083 in NaCl solutions by increasing the amount of $CeCl_3$. Up to 500 ppm of $CeCl_3$, a progressive decrease of E_{corr} and i_{corr} is observed. Higher values of inhibitor concentration return the diagram to upper right positions.

persive Spectroscopy (EDS) techniques were used in order to get some additional data concerning the inhibition mechanism. The SEM image of Fig. 4 shows that on the surface of a sample of AA5083, after a full immersion test of 30 days in 3.5% NaCl aerated solution with 500 ppm of $CeCl_3$, a thin film is developed. The EDS spectrum of Fig. 5 contains peaks characteristic of cerium. This data clearly confirms the incorporation of the lanthanide ion into the protective film, as can be expected for a typical cathodic inhibitor. Taking into account the absence of Cl in the EDS spectrum and the well-established acid-base behaviour of lanthanide ions it seems likely that the film-forming process takes place by precipitation of lanthanide oxide or hydroxide on the cathodic sites of the metallic surface, where as a consequence of the cathodic reactions, locally high hydroxide anion concentrations exist. Similar results have been already reported in studies of the inhibition behaviour of lanthanide salts on different aluminium alloys [5,9,11,15] and steels [3].

Fig. 4. SEM image recorded on a sample after a 30 days full immersion test in a 3.5% NaCl solution containing 500 ppm of added $CeCl_3$.

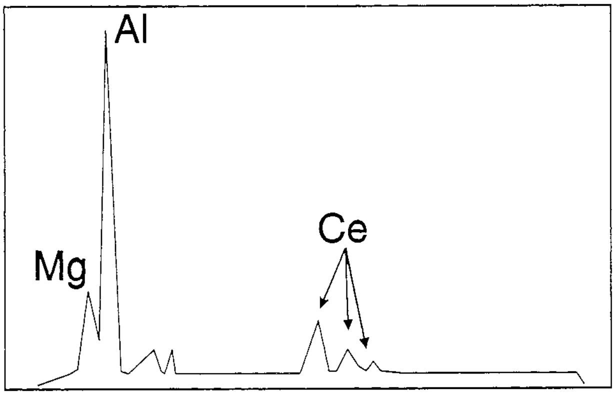

Fig. 5. EDS spectrum recorded in the region imaged in Figure 4.

On the other hand, polarisation curves allow us to estimate the corrosion rate, using ParcCalc Routine of M352 Corrosion Software, from the measurement of the current density value observed at E_{corr}. Fig. 6 plots corrosion rates, obtained using this procedure, as a function of lanthanide salt concentration. A large decrease in corrosion rate can be clearly noticed, even for the lowest inhibitor concentration values. These results parallel those recorded in Fig. 1 coming from conventional tests. In most cases, the corrosion rate is reduced by more than 90%, a factor similar to that observed with Cr(VI) based classical inhibitors. Although no drastic differences can be stated between the tested lanthanide salts, additions of 500 ppm of $CeCl_3$ or $SmCl_3$ provided the highest protection degree against uniform corrosion.

The second aim of the present work was to determine the inhibition power of the lanthanide salts against pitting corrosion, possibly the most serious corrosion phenomena

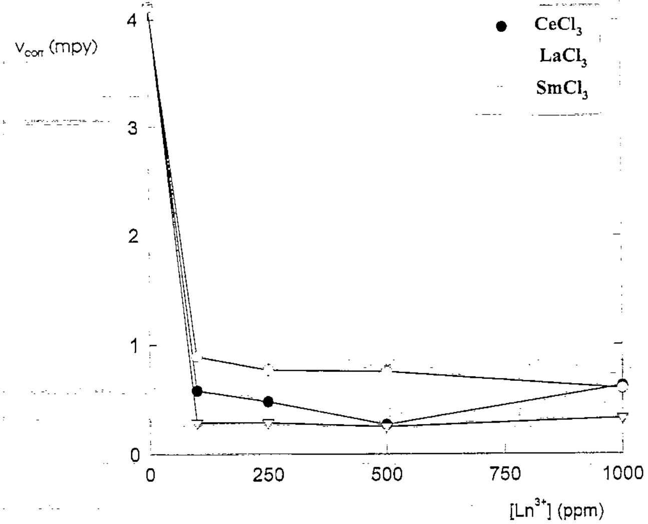

Fig. 6. Evolution of v_{corr} values obtained from linear polarisation curves as a function of Ln^{3+} ion concentration. Note the steep decrease in the corrosion rate even for small amounts of added lanthanide salt. The dependence of corrosion rate on inhibitor is quite similar for the three salts studied here.

of this alloy in NaCl solutions [17]. In order to evaluate the intensity of the pitting process "samples free from corrosion products" coming from full immersion tests, were examined using a scanning electron microscope. Fig. 7(A) shows the SEM micrograph depicting the appearance of a sample tested in aerated 3.5% NaCl solution after 30 days exposure. A large density of pits can be observed with an average diameter close to 10 μm. In contrast to this, no pits are observed in SEM images of samples tested, under the same experimental conditions, in $LnCl_3$–containing solutions, Fig. 7(B). This result suggests that the lanthanide salts can also play an important role as pitting corrosion inhibitors.

To get a further insight into the pitting corrosion process, cyclic polarisation measurements were used, Fig. 8. This technique has allowed us to determine the degree of protection against pitting corrosion supplied by the lanthanide compounds as well as their influence on the characteristic steps of this form of localised attack, i.e. nucleation of new pits and growth of pre-existing pits.

As stated above, two factors should contribute to the overall pitting corrosion resistance. First, the resistance against the nucleation of pits and, secondly, a growth resistance. The former has been evaluated as the difference, R, between the pitting potential, E_{pit}, and the corrosion potential E_{corr} [18]. Though this R parameter cannot be used in absolute terms, it is very useful when used as a comparative parameter. Thus, a higher R value indicates a higher resistance against pit nucleation. With this in mind, the protection degree against pitting nucleation, P_{pit}, was estimated in terms of the percentage increase of R, taking as reference the value of this parameter observed in the cyclic polarisation experiment carried out in the bare NaCl solution, R^0.

The resistance against growth of pre-existing pits was evaluated by comparing the areas of the anodic hysteresis loops observed in the cyclic polarisation diagrams plotted in i–E style. This area is related to the electrochemical power consumed during the growth of the pre-existing pits. The percentage decrease of this area, from the value observed for the bare NaCl solution, was taken as a measurement of the protection degree against pitting growth.

Fig. 7. SEM micrographs obtained from an AA5083 sample after 30-day full immersion tests in (A) bare 3.5% NaCl solution and (B) 500 ppm $CeCl_3$–3.5% NaCl solution. The latter was recorded after properly cleaning the surface of the sample shown in Figure 4.

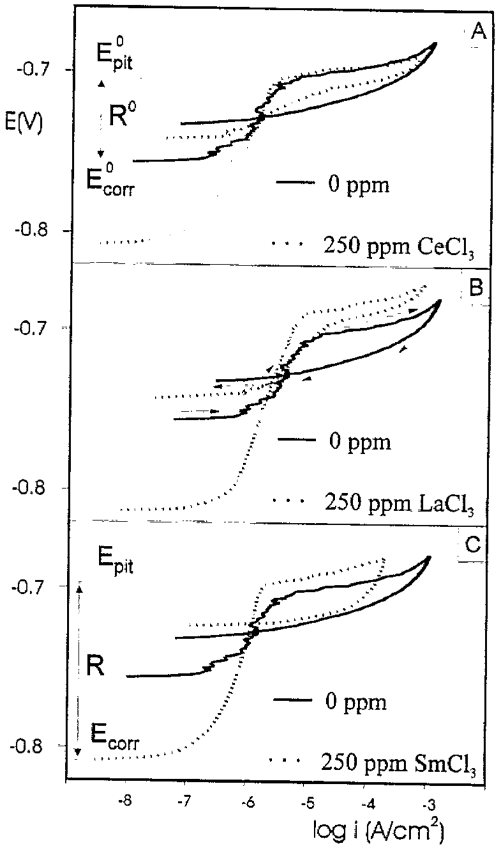

Fig. 8. Cyclic polarisation diagrams for AA5083 in bare NaCl solution and with 250 ppm additions of (A) $CeCl_3$, (B) $LaCl_3$ and (C) $SmCl_3$. Pit nucleation resistance can be evaluated by the difference between the pitting potential (E_{pit}) and the corrosion potential (E_{corr}). The 0-superscripts values in the figure are those corresponding to the absence of inhibitor. Note that the addition of $LnCl_3$ increases the resistance.

Fig. 8 shows the cyclic polarisation curves of AA5083 alloy in 3.5% NaCl without (solid line) and with (dashed lines) a 250 ppm addition of $LnCl_3$. It can be observed that the presence of lanthanide chlorides affects mainly the value of the corrosion potential, while the pitting potential remains, in the three cases here studied, nearly constant. This decrease in E_{corr} gives rise to a large increase in the pitting nucleation resistance, R, when the samples are in the presence of $LnCl_3$. Fig. 9 shows the degree of protection against pitting nucleation, P_{pit}, as a function of inhibitor concentration for the three salts studied. The highest inhibition effect is observed for 500 ppm additions of $CeCl_3$. It is worth noting also the steep decrease of P_{pit} recorded for the solution containing 500 ppm $SmCl_3$. The origin of this special behaviour of Sm is still not well established, this being one aspect that deserves further investigation. Nevertheless, it is likely that a synergistic effect between the high chloride concentration and the chemical properties of samarium, different from those of cerium and lanthanum, could be responsible for this result.

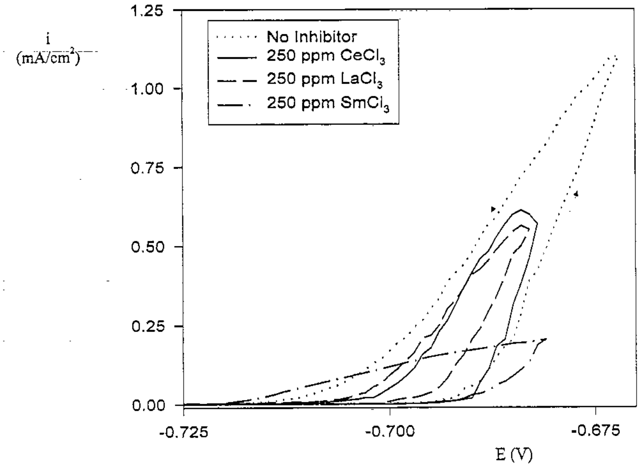

Fig. 10. The same curves shown in Figure 8 but plotted in i–E style. The areas inside the anodic hysteresis loops are a measurement of the power expended in the growth of pre-existing pits.

Fig. 10 shows the cyclic polarisation curves included in Fig. 8, now plotted in i–E style. Note that in this case also the samarium salt shows a different behaviour, this fact suggesting that a particular protection mechanism could be in action for $SmCl_3$. Using a specific routine of the M352 Corrosion Software, the areas of the anodic hysteresis loops were calculated. From these values the percentage of decrease of spent power, P_g, can be calculated, Fig. 11. The P_g parameter can be used as a measurement of the resistance against pitting growth. The best protection degree was found with 500 ppm additions of $LaCl_3$ or $CeCl_3$.

In summary, additions of $LnCl_3$ salts to NaCl media result in an improved behaviour against pitting corrosion of AA5083 aluminium alloy. The optimum amount of inhibitor is around 500 ppm. For this value $CeCl_3$ can be considered as the compound with the best performance, given that the other two chlorides investigated present a lower resistance against pit nucleation for this inhibitor concentration.

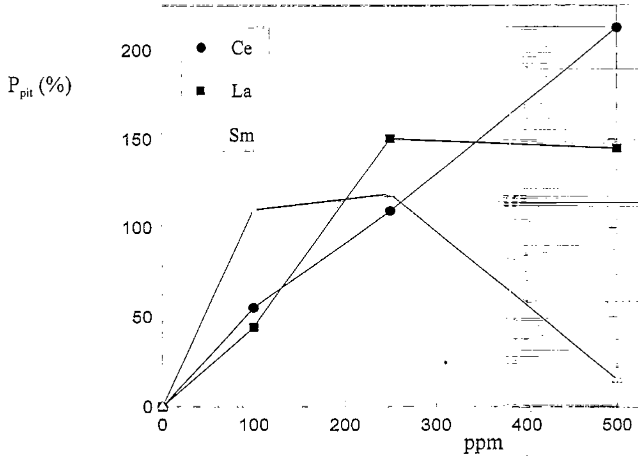

Fig. 9. Estimated values of the degree of protection against pit nucleation as a function of Ln^{3+} concentration.

4. Conclusions

Weight loss and electrochemical linear polarisation data indicate that lanthanum, cerium and samarium chlorides are effective uniform corrosion inhibitors of AA5083 aluminium alloy in 3.5% NaCl aerated aqueous solution, at room temperature. Moreover, the absence of pits in samples immersed into solutions containing $LnCl_3$, permits us to conclude that these salts also act as pitting corrosion inhibitors.

The protection factors against uniform corrosion obtained from linear polarisation data are of the same order as those found with classical Cr(VI) based compounds. This fact, combined with the low toxicity of the lanthanide salts allows us to consider them as an efficient and ecological alternative to chromate inhibitors.

Linear polarisation curves suggest a cathodic character for the inhibition process. In this sense, the inhibition process would take place by precipitation of lanthanide oxide or hydroxide on the cathodic sites of the metallic surface, finally forming a protective film as revealed by SEM and EDS. This film acts as a barrier between the metal and the aggressive media, blocking the cathodic reaction and, therefore, decreasing the corrosion rate.

Data extracted from cyclic polarisation tests have allowed us to determine the degree of protection against pitting corrosion. In general, the presence of $LnCl_3$ in the 3.5% NaCl solution increases the pit nucleation and growth resistance. Protection factors over 200% have been found for the former parameter while, for the second, the

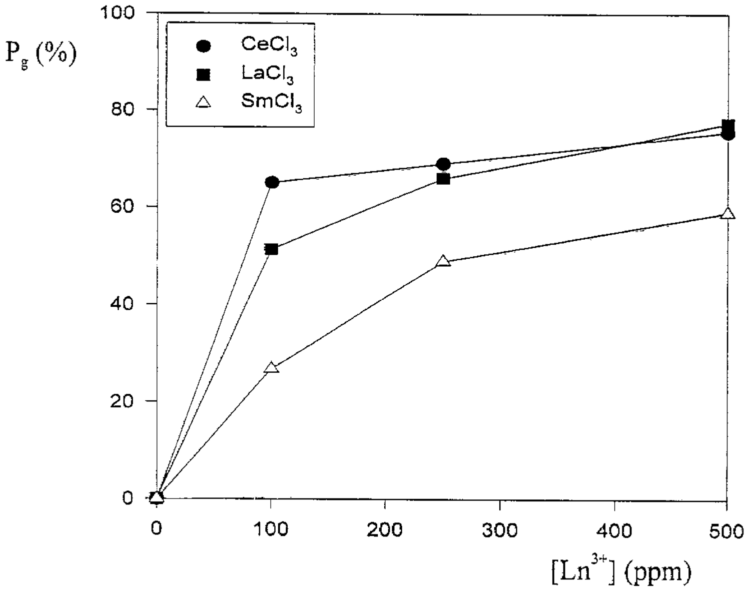

Fig. 11. Degree of protection values against pit growth as a function of inhibitor concentration.

maximum value is around 70%. The best performances have been obtained for 500 ppm additions of $CeCl_3$.

Acknowledgments

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