CORROSION EVALUATION ADVANCES FOR PROMISING TES MATERIALS IN ALUMINA FORMING ALLOYS

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Abstract

In the present study, new molten-salts are being proposed for Thermal Energy Storage (TES) materials at high temperature, but their corrosion characteristics are not available in the literature. The corrosion issues have to be resolved completely before commercial application of the molten-salts as the HTF in CSP plants.

To mitigate corrosion, different alumina forming alloys have been exposed to the most promising molten salts to be proposed for the new storage trends in CSP plants. This paper includes an extended corrosion study for these new developments, including nitrate, carbonate and chloride molten salts.

Ni base steels showed a better behavior in the corrosive environments and electrochemical impedance tests showed the formation of a protective layer in the first 24 hours.

The gravimetric results and SEM analyses that were performed, confirm the excellent behavior of the steels tested in nitrates and carbonates salts reducing the corrosion ability in these promising novel molten salts compared with the solar salt currently used in solar technology.

On the other hand chloride molten salt presents a very aggressive environment and the steels proposed are not recommended for its use as container materials in CSP plants.

Keywords: *Thermal Energy Storage, Molten Salt, Corrosion, Electrochemical Impedance Spectroscopy*

1. Introduction

High temperature corrosion is one of the most important issues for materials selection, structure design and service life prediction of engineering parts which are exposed to high-temperature enviroments. The prevention of high temperature corrosive attacks on materials play a critical role in aspects such as reliability, quality, safety and profitability of any industrial sector associated with high temperature process and in the study case, solar energy storage market, using inorganic molten salt (Vignarooban, Xu et al.).

Solar power tower technology is the current and future trend for CSP installation, because of its potential to achieve very high temperatures which leads to enhanced efficiency of converting heat into electricity.

The operating temperature range in the currently available solar power tower plants is between 300 and 565 C. In the future, even higher operating temperature up to 800^0C are anticipated (Kruizenga 2012). In this context, only molten-salts with extremely high boiling points can be used in the forthcoming solar power tower plants. Other possibility is reduce melting point in current molten nitrate salts in order to increase the work temperature range (Wang, Mantha et al.; Fernandez, Ushak et al. 2014). In this direction, LiNO3 is the most promising candidate and it´s eutectic formulation will be study in this paper.

It is known that Electrochemical Impedance Spectroscopy (EIS) is a powerful technique that has been used to determine corrosion mechanisms in aqueous corrosion of alloys and metals for decades. The method has gained popularity since it can be performed in-situ, and also because it usually doesn't require any artificial acceleration of the corrosion process (Vidal 2014). The greatest advantage of this technique is the low intensity of excitation signal used which causes minimal disruption in the electrochemical system state, constituting a non-destructive technique and reducing the error associated with the measurement process. Impedance spectra obtained by this method are adjusted to an electrical circuit of a combination of resistors and capacitors (equivalent circuits), in order to interpret the corrosion processes.

This research is focus on corrosion ability of different thermal storage materials due to is one of the critical components for transferring thermal energy in concentrating solar power systems. Various types of thermal storage materials including nitrates, carbonates and chlorides have been selected in order to discuss the better materials for avoid corrosion issues in future developments.

The selected salts were the most promising candidates to be use in the new generation of CSP plants:

- 30wt% $LiNO_3$ + 57wt% KNO_3 + 13wt% $NaNO_3$

- 32wt% Li_2CO_3 + 33wt% Na_2CO_3 + 35wt% K_2CO_3

- 45wt% LiCl + 55wt% KCl

The corrosion tests were carried out at 550°C (nitrates), 650°C (carbonates) and 750°C (chlorides) during 1000 hours.

Regarding the materials selected, in the last years Oak Ridge National Laboratories (ORNL) have explored the effects of alloying additions on oxidation and creep behavior with an emphasis on the variation of Nb content as a function of Ni and Al levels. Niobium additions is an important factor in oxidation resistance because increase niobium and nickel levels may reduce alloy oxygen solubility, which favors external protective Al_2O_3 scale formation (Brady, Yamamoto et al. 2007) with a superior degree of protection that Cr_2O_3.

The AFA alloys show a promising combination of oxidation resistance, creep resistance, tensile properties and potential for good welding behavior. The optimal alloy composition appears in the range of (20-25%)Ni-(12-15%)Cr-(3-4%)Al-(1-3%)Nb wt% base, with a temperature limit from an oxidation standpoint approaching 9000C for alloy compositions at the higher aluminum, niobium and nickel contents of the range. The steels selected for this research are shown in table 1.

Tab. 1: Chemical composition of the steels tested in molten salts

Steels	Weight (%)							
	Al	Mn	Ni	Cr	Mo	Ti	Nb	Fe
AISI 304	-	1.7	8.04	18,28	0.27	0.01	0.008	Balance
OC-4	3.5	2	25	14	2	0.1	2.5	Balance
OC-T	3	-	35	14	-	2	3	Balance
In 702	2.7-3.7	-	75	14-17	-	-	-	2
HR224	3.2	-	47	21	-	-	-	27.5

2. Procedures

The saline nitrates that were used in the research were $NaNO_3$, KNO_3 and $LiNO_3$ (Merck 98%). The dimensions of the analyzed samples in the gravimetric corrosion tests are 20 mm × 10 mm × 2 mm; the dimensions of each sample were measured using an electronic caliber, and each sample was weighed using an analytical balance with a 0.00001 g responsiveness. Subsequently, the samples were placed in alumina crucibles with the saline mixture and then were heated in a resistance oven at 550°C-650°C-

750°C. Gravimetric measurements were performed at 170, 335, 500, 675, 850, 1000h of the analysis for the isothermal immersion test. After the samples were removed from the oven, they were slowly cooled in warm distilled water to eliminate the salt in which they were immersed. Next, they were dried and weighed, with the average value of the weight obtained from five weight values. The formula (Eq. [1]) to calculate the mass gain over time is:

$$\frac{\Delta m}{S_0} = \frac{m_f - m_i}{S_0} \qquad \text{(Eq 1)}$$

where m_i is the initial mass of the specimen, m_f is the mass of the same at time t and S_0 is the initial area of the specimen.

The same procedure was following for carbonate salts Li_2CO_3, Na_2CO_3 and K_2CO_3 (Merk 98%) but in this case the samples was cleaned after immersion using a clark solution 10% H_2SO_4 in order to remove the salt remaining. This procedure was also used in chloride molten salt: LiCl, KCl (Merk 98%).

PPS and OCP were used to determine the Tafel slopes and corrosion rates of steels tested after immersion in molten 45wt% LiCl + 55wt% KCl at 750°C. EIS was employed to determine the corrosion mechanisms. Down selection of the best conditions per alloy was performed based on corrosion rates obtained from PPS tests. Nyquist plots obtained with time were employed to determine the corrosion mechanism change.

A two-electrode arrangement was used with the working electrode (WE) as the sample, the reference electrode (RE) and the counter electrode (CE) were connected in the same sample. The electrochemical tests were performed using a potentiostat (AUTOLAB–PGSTAT302N).

For the PPS experiments, the WE' potential (E) was continuously recorded starting immediately after its salt' immersion until dE/dt ≤ 100 µV/s was obtained and thus OCP was stablished. PPS test was conducted immediately after by applying cathodic (–) and anodic (+) external potentials from –0.35 V to +0.6 V around the OCP or corrosion potential at 0.001 V steps and 0.001 V/s. More than five coupons per test were performed under the same conditions to evaluate the reproducibility of the results. Some results were discarded based on PPS curve behavior. The corrosion current density, jcorr, was calculated from the intersection of the extrapolated straight sections of the cathodic and anodic Tafel slopes within an interval of 120 mV with respect to Ecorr.

3. Results

The steels tested in lithium nitrate salt at 550ºC were stainless steels, Inconel and AFA alloys (OC-4 and OC-T) with compositions presented in table 1; the steels were immersed in the molten salt for 1000 hours. The gravimetric gain that occurred in these steels is shown in figure 1.
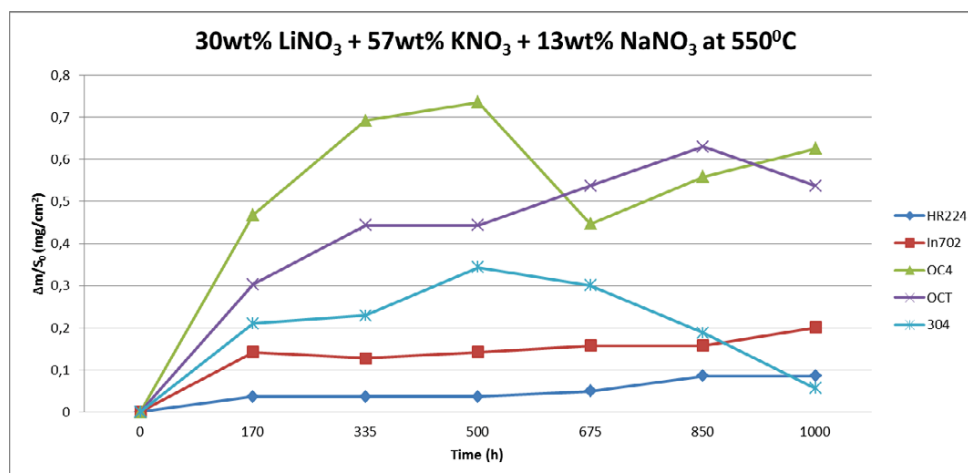

Figure 1: Gravimetric corrosion curve in saline 30%LiNO$_3$ +57%KNO$_3$ + 13%NaNO$_3$ at 550C for 1000 hours of test

The OC steels (with Al content) show higher mass gain after 1000 hours of saline exposition, resulting in an irregular growth of mass, with different weight gains and losses. In contrast, In702 and HR224 show the best behavior in this environment with a reduced mass gain.

It is important to point out the weight gain in 304SS with a linear corrosion rate until 500h of exposure and a change on this trend at the end of the experiment.

To explain this behavior, a micro-structural (superficial) study of the 304 stainless steel was performed using Scanning Electron Microscopy (SEM). Figure 2 shows the superficial appearance of the sample after 500 and 1000 hours of exposure as well as the EDX analysis performed.

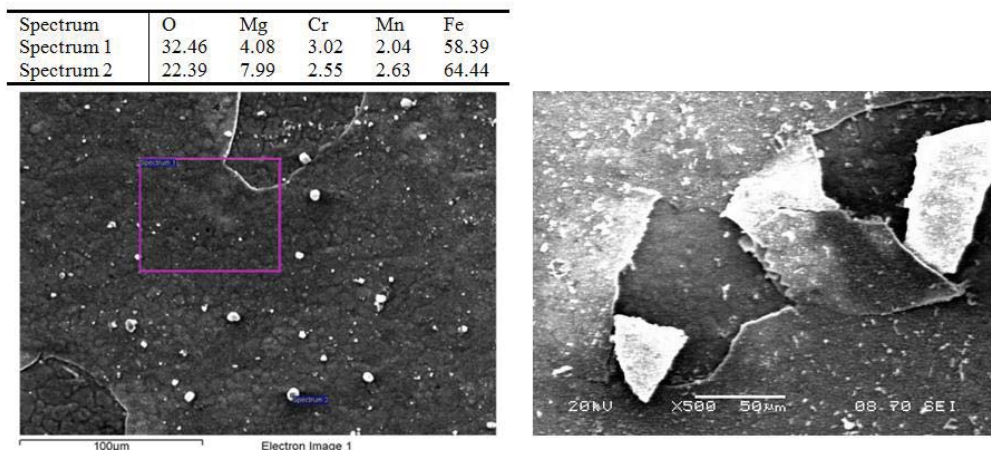| Spectrum	O	Mg	Cr	Mn	Fe
Spectrum 1	32.46	4.08	3.02	2.04	58.39
Spectrum 2	22.39	7.99	2.55	2.63	64.44

Figure 2: Superficial image of 304SS at left) 500 h and right) 1000h of test

The formed oxidation layer is very fragile, with several releasing zones, which explains the continuous fluctuations in the mass gain and the weight reduction at the end of the test.

HR224 (figure 3 left) and In702 (figure 3 right) showed the best behavior against corrosion due to the formation of a protective alumina scale.

Spectrum	O	Mg	Al	Cr	Fe	Ni
Spectrum 1	29.93	4.63	4.92	12.12	28.91	18.69
Spectrum 2	31.37	5.92	2.60	7.06	41.29	11.52
Spectrum 3	40.29	46.60	0.74	0.82	9.00	2.43

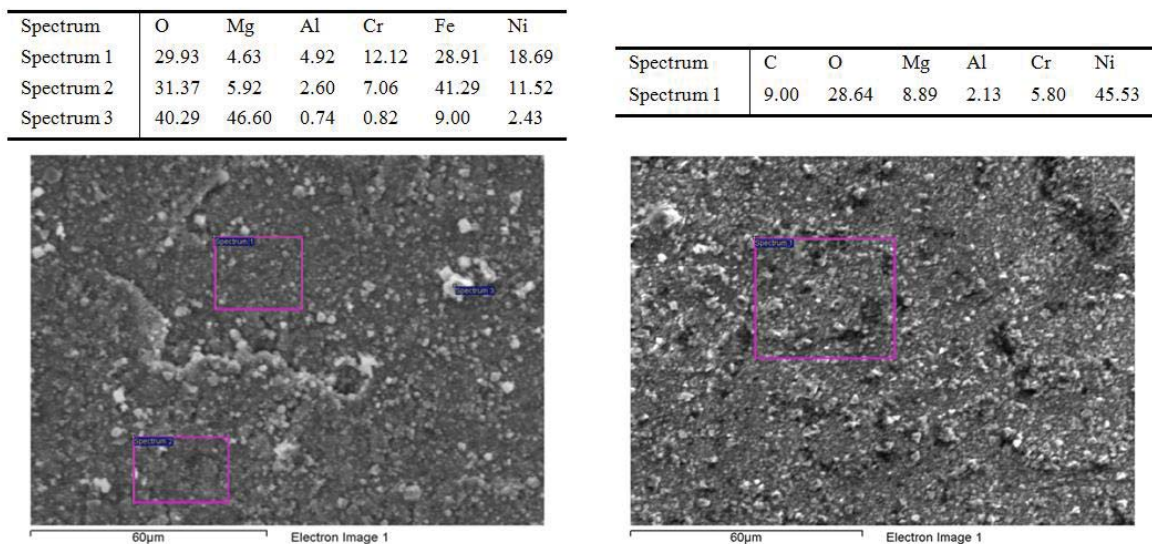| Spectrum	C	O	Mg	Al	Cr	Ni
Spectrum 1	9.00	28.64	8.89	2.13	5.80	45.53

Figure 3: Superficial image of left) HR224 and right) In702 at 1000h of test

HR224 showed a higher Al and Cr content compared with In702 explaining the best behavior in the corrosive environment.

The steels tested in lithium carbonate salt at 650°C were, the same alloys, 304SS, Inconels and AFA alloys (OC-4 and OC-T) with compositions presented in table 1; the steels were also immersed in the molten salt for 1000 hours. The gravimetric gain that occurred in these steels is shown in figure 4.
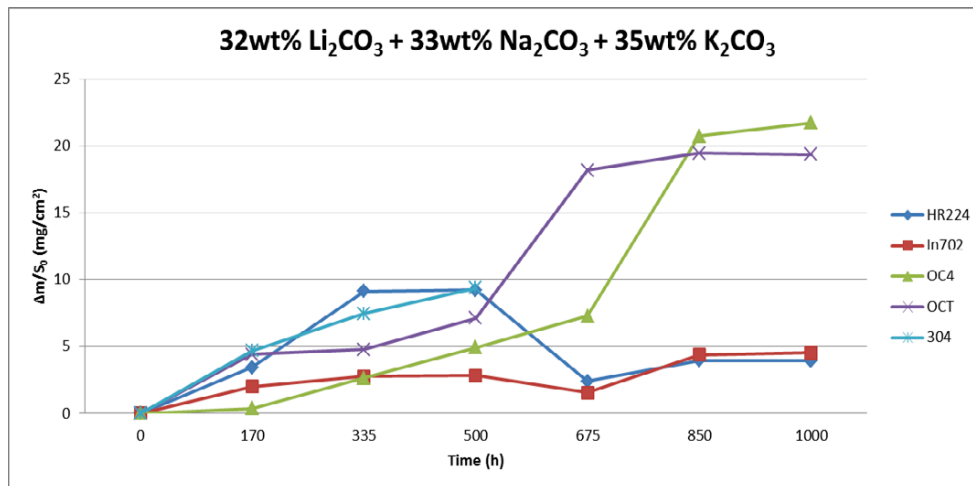
Figure 4: Gravimetric corrosion curve in saline $32\%Li2CO_3 + 35\%K2CO_3 + 33\%Na2CO_3$ at 650C for 1000 hours of test

Corrosion rate showed a higher increase compared with nitrate molten salts. 304SS test only could be carried out until 500 hours of immersion, showing a severe and catastrophic corrosion spallation (fig 5).

Figure 5: Corrosion observed in 304SS immersed in saline $32\%Li_2CO_3 + 35\%K_2CO_3 + 33\%Na_2CO_3$ at 650C during 500 hours of test

AFA alloys, OC4 (figure 6 left) and OCT (figure 6 right) showed the higher mass gain in contact with carbonate molten salt studied. The superficial study revealed small Al_2O_3 particles on OC4 surface that not offer a complete protection in the steel. Superficial study on OCT steel revealed an unprotective $MgFe_2O_4$ scale.
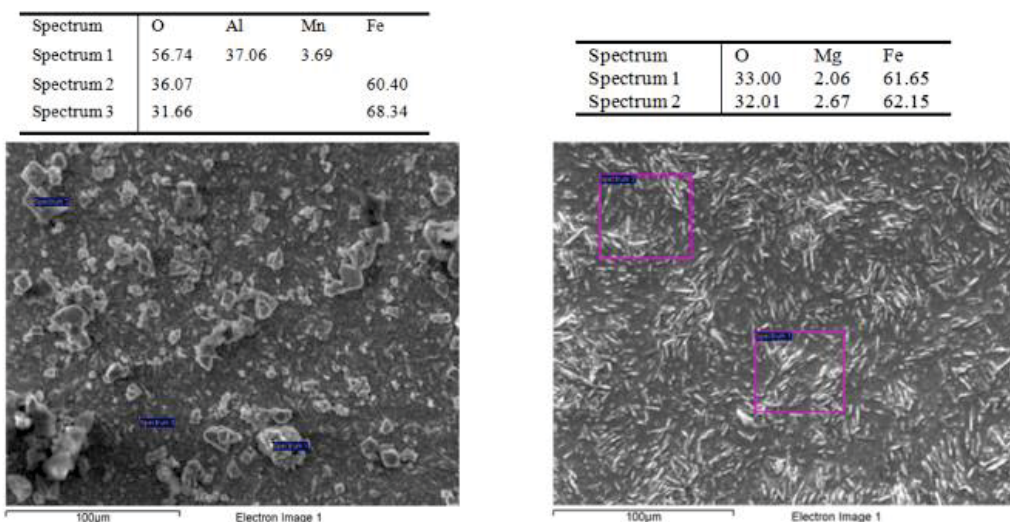
Spectrum	O	Al	Mn	Fe
Spectrum 1	56.74	37.06	3.69	
Spectrum 2	36.07			60.40
Spectrum 3	31.66			68.34

Spectrum	O	Mg	Fe
Spectrum 1	33.00	2.06	61.65
Spectrum 2	32.01	2.67	62.15

Figure 6 Superficial image of left) OC4 and right) OCT immersed in saline 32%Li2CO$_3$ +35%K2CO$_3$ + 33%Na2CO$_3$ at 650C during 1000 hours of test

HR224 and In702 shoed the best behavior against carbonate corrosion and, in this case, are forming a protective Al-O-Ni scale in the steel surface (Fig 7)
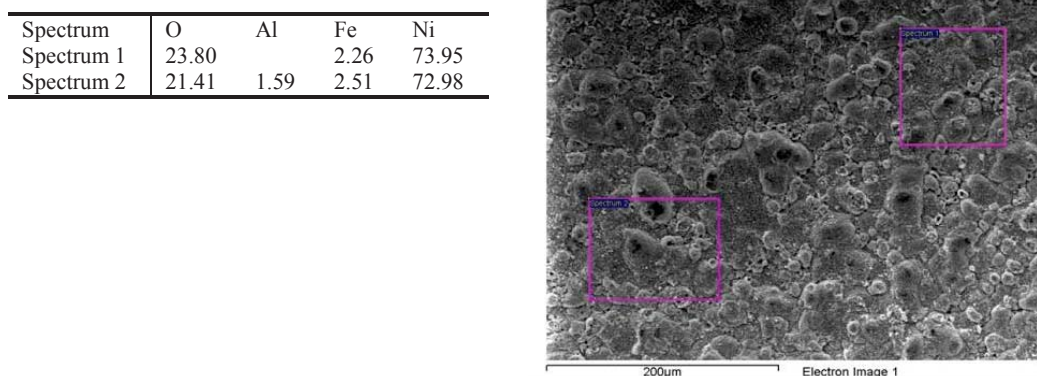
Spectrum	O	Al	Fe	Ni
Spectrum 1	23.80		2.26	73.95
Spectrum 2	21.41	1.59	2.51	72.98

Figure 7: Superficial image of In702 immersed in saline 32%Li$_2$CO$_3$ +35%K$_2$CO$_3$ + 33%Na$_2$CO$_3$ at 650C during 1000 hours of test

According with results obtained, the corrosion study on chloride molten salt at 750^{0}C was only performed on HR224 and In702. The gravimetric results obtained are shown in figure 8.
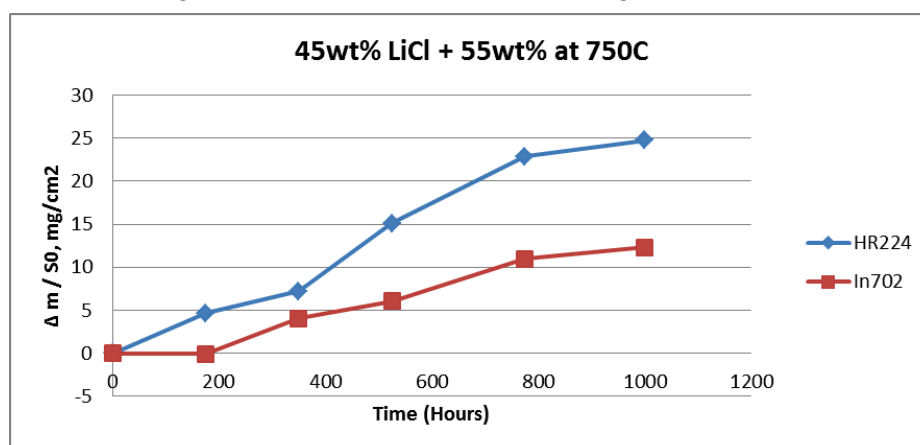

Figure 8: Gravimetric corrosion curve in saline 45%LiCl + 55%KCl at 750C for 1000 hours of test

In this case, In702 showed a lower mass gain compared with HR224 and this molten salt was the most corrosive tested in this study. Some EIS test has been developed in chloride molten salt in order to obtain corrosion rates and mechanism.

PPS and OCP were used to determine the Tafel slopes and corrosion rates of steels. Results are shown in table 2.

Tab. 2: PPS and OCP results obtained in EIS test

Alloy	Area immersed	CR, mm/y	Polarization Resistance	Test Temperature	OCP (LSV)	E corr
HR224	2,32412	0,93039	124,05	750	-0,348	-0,426
In 702	1,95158	0,61475	297,07	750	-0,414	-0,54

This technique was also used for monitorize the corrosion and Nyquist diagrams were obtained for In702 at 24 and 100h.
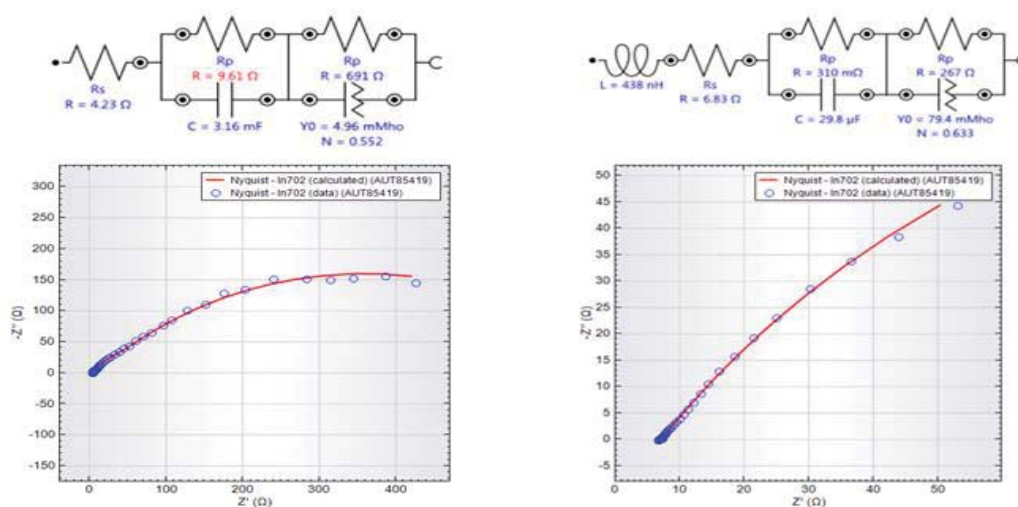

Figure 9: Nyquist diagrams for EIS study performed in saline 45%LiCl + 55%KCl at 750C for left) 24 h and right) 100 h of test

To fit the data, corrosion models in molten salts must be used. In this case, the Nyquist plots and their respective equivalent circuits are matching for a protective layer (fig 9 left) and localized corrosion model (fig 9 right).

Two semicircles are typical of protective layers and the latter type is produced by the rupture of protective layers which initiates pits creating a localized corrosion.

4. Conclusion:

Molten salts act as the electrolyte in a corrosive system that attacks the metal containers. High operating temperature is necessary to improve efficiency in the CSP system and molten-salts are the most promising TES materials at high temperatures. Different Alumina Forming Austenitic (AFA) steels have been proposed as container and pipping materials, HR224 and In702 showed the best corrosion resistance in the molten salt tested. On the other hand, their use it is not recommended for container material in storage tanks involving chloride molten salt.

Acknowledgements

5. References

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