Thermal characterisation of an innovative quaternary molten nitrate mixture for energy storage in CSP plants

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ABSTRACT

Enhancements to energy storage systems developed for solar thermoelectric technologies can yield considerable increases in efficiency for this type of renewable energy. Important improvements include the design of innovative storage fluids, such as molten salts possessing low melting points and high thermal stabilities.

This research examines the design of an innovative quaternary molten nitrate mixture, with the goal of improving the solar salt used currently as an energy storage fluid in CSP plants. This quaternary salt, which contains different weight percentages of $NaNO_3$, KNO_3, $LiNO_3$ and $Ca(NO_3)_2$, exhibits better physical and chemical properties than the binary solar salt (60% $NaNO_3$ + 40% KNO_3) currently used. The melting points, heat capacities and thermal stability of the quaternary mixtures were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition to DSC and TGA tests, viscosity and electrical conductivity measurements were carried out for the quaternary mixtures at different temperatures.

The new salt was designed by taking into consideration the risk of solid species formation at high temperatures when calcium nitrate is present (which requires that the wt% does not exceed 20%) and the costs of $LiNO_3$. These boundaries set the maximum wt% of $LiNO_3$ to values below 15%.

Finally it was determined that the proposed quaternary mixture, when used as a heat transfer fluid (HTF) in parabolic trough solar power plants, is able to expand plants' operating range to temperatures between 132 and 580 °C.

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1. Introduction

In recent years, the study of renewable energy and its practical applications has greatly expanded. Solar energy is one of the technologies that has benefited most from international commitments geared toward reducing and controlling the emissions of CO_2 from energy storage systems. Several research topics in this field address the development of methods for enhancing the performance of solar plants under unfavourable weather conditions or at night. Modern solar technology has an extremely positive energy balance, given that the CO_2 emissions generated from fabrication, installation and servicing over a solar turbine's average operation life of 20 years are covered after the first 3–6 months.

In the context of advanced industrial development and with high levels of energy efficiency, Concentrated Solar Thermal Energy (CSTE) could supply up to 7% of global energy needs by 2030 and 25% by 2050 [1].

An important component of Thermal Energy Storage (TES) systems is the choice of heat transfer fluids used in a solar plant. The main challenges to electrical power generation from solar thermal plants with more profit are the following:

- reducing the investment, operational and maintenance costs;
- extending the hours of operation and energy supply;
- increasing the temperatures in the thermal cycle;
- increasing the lifetime of power plants.

Research and development in the solar energy sector has focused on reducing the high cost associated with the operation

and maintenance of these plants. One of the most important lines of research in this respect is the study, design and characterisation of the salts that are used as energy storage fluids.

The objective of our study was to design new salt mixtures that can replace the current binary salt (composed of 60% NaNO$_3$+40% KNO$_3$) used in energy storage systems [2,3], given that maintaining the tanks and system of pipes through which this binary mixture circulates above its freezing point (223 °C) constitutes a significant proportion of the energy required to run solar energy plants.

The potential for improving the salt resides in optimising its physiochemical properties, mainly its melting point, thermal stability and heat capacity, by developing new quaternary mixtures or by incorporating novel components. Raade et al. [4] presented mixtures with up to five components and diverse compositions and introduced caesium nitrate to mixtures reported in the literature, succeeding in reducing the melting point to 70 °C. However, the cost of CsNO$_3$ (which is even greater than that of LiNO$_3$) makes these mixtures commercially unviable. The same researchers have recently designed new formulations chosen among thousands of compositions that allow the reduction of the melting point to below 60 °C [5]. The proposed material, which includes a KCl component, can cause problems through corrosion to the salt storage tanks. The proposed nitrate content also presents some drawbacks, as it is necessary to control the atmosphere in contact with the salt to prevent nitrate oxidation. These considerations suggest that these salts are also not commercially viable.

In light of several studies [6–10] that have involved the addition of Ca(NO$_3$)$_2$ and LiNO$_3$, our research proposes a new quaternary mixture with a composition of 10% LiNO$_3$+20% NaNO$_3$+60% KNO$_3$+10% Ca(NO$_3$)$_2$. This quaternary mixture was designed by taking into account the commercial requirements of the solar energy market. For this reason the maximum contents of LiNO$_3$ and Ca(NO$_3$)$_2$ do not exceed 10% owing to the materials' high cost and the limitations associated with operating at high temperatures, which requires greater quantities of calcium nitrate.

The melting point, maximum thermal stability and heat capacity of the proposed mixture were obtained by thermal characterisation (DSC, TGA and MDSC). Additionally, we studied the viscosity levels at temperatures near the melting point with the objective of identifying the lowest temperature at which the newly designed salts can properly flow through the pipes in a solar power plant.

The novelty of this study lies in the implementation of a process that uses an electrochemical impedance technique to determine the electrical conductivity of the target salt. Theoretical models were employed to interpret the impedance spectra, allowing for the impedance to be calculated as a function of the frequency. These models were used to simulate the electrical behaviour of the system based on the electrolytes and the electrolyte–electrode interphases [11,12].

A functional electrochemical cell can be represented by an equivalent circuit composed of a set of passive elements that reproduce the behaviour of a material when it corrodes [13]. These circuits allow the impedance to be related to the chemical process responsible for the behaviour of the system. In this context the horizontal axis of a Nyquist diagram represents the real part of the impedance, and the vertical axis represents the imaginary part of the impedance at two different frequencies [14]. The semicircle obtained from a parallel RC circuit (Fig. 1) is used for values greater than Z' to express the total impedance of the Randles circuit:

$$Z = R_s + \frac{1}{\frac{1}{R_{ct}}+jw\,C_{dl}} \qquad (1)$$

where R_s is the resistance to dissolution, R_{ct} is the resistance to charge transference and C_{dl} is the capacitance of the double layer.
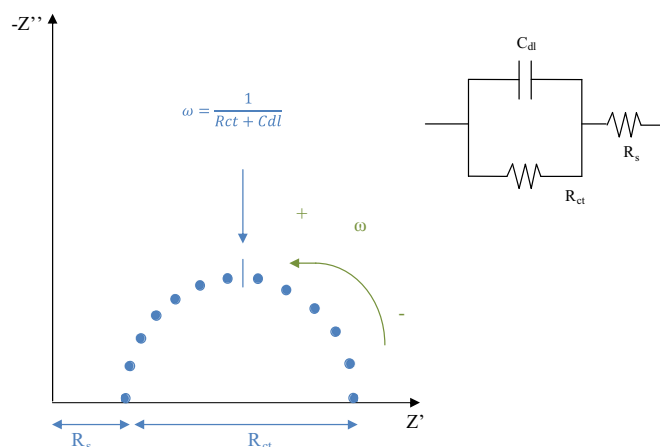

Fig. 1. Nyquist squeme of a Randles circuit.

This technique has been used to determine the resistivity of nitrate salts (R_s) because these salts exhibit high electrical conductivity [15].

Additionally, it is important to know the electronic properties of a salt at the appropriate storage temperatures to improve the thermal conversion ratio in solar plant heat exchangers.

2. Material and methods

The nitrate salts used in the study were NaNO$_3$ and KNO$_3$ (Sigma-Aldrich 98%) as well as Ca(NO$_3$)$_2\cdot$4H$_2$O and LiNO$_3$ (Panreac 98%). The pre-melted and solidified mixtures were analysed to determine their heat capacities and to study their fusion characteristics (DSC) and thermal stability (TGA). A combination of the anhydrous and tetrahydrate forms of nitrate was chosen to ensure the proper elimination of water and to study the corresponding effects on the salts. Following the thermal treatment, the salts were carefully handled to avoid water absorption, and the mixed formulation was sealed inside a dry box containing desiccants.

Thermal assays were conducted with a Mettler Toledo calorimeter capable of simultaneous thermogravimetric readings to obtain thermal decomposition curves for the designed salt. Additionally, a DSC-Q20 calorimeter was used to obtain a pure DSC signal to determine the heat of fusion, melting point and Cp at 390 °C. This test (MDSC) lasted 40 min. The temperature was modulated by $\pm$0.5 °C every 130 s around the working temperature of 390 °C. The sample was perfused before the tests to eliminate any excess water and thus obtain the most precise measurements.

Two different crucibles were employed. The crucibles used in the TGA instrument were made of platinum, whereas the crucibles used in the DSC Q-20 instrument were made of aluminium and were hermetically sealed. Both tests were conducted in a flowing inert nitrogen atmosphere (50 ml/min) and at a heating rate of 10 °C/min. The equipment was calibrated with indium (TGA and DSC analysis) and sapphire for the MDSC study. The typical sample mass was 10 mg.

To study the viscosity of the new quaternary salt, measurements were performed at temperatures of 150, 175, 200 and 300 °C using a rheometer coupled with a Peltier plate (TA instruments). The Peltier plate (below) heated the salt to the desired working temperature whereas the upper platform (above) was superimposed on the sample and subjected to a shear rate of 100 s^{-1}, which allowed for the determination of the viscosity of the material by measuring the degree of flow resistance.

A special experimental setup was required to measure the electrical conductivity by electrochemical impedance spectroscopy (EIS). To perform the electrochemical measurements, stainless