

Stability of Nickel Compounds in Molten Carbonate Fuel Cell

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Abstract: Molten carbonate fuel cell (MCFC) has attracted much attention as a large-scale civil power generation device. However, there are some defects in MCFC. The cathode material NiO will dissolve slowly in high temperature molten salt electrolyte with a long time, and the metal Ni will precipitate on the surface of the cathode and form a bridge with the metal Ni of the anode material, thus resulting in short circuit of the battery. Experiments show that the service life of batteries can be improved by using new rare earth electrode materials and changing the composition of carbonate electrolyte.

1. Introduction

The rapid development of the world has brought many problems such as the warming of the earth, lack of energy, destruction of the environment and so on. While a large amount of energy is consumed, the emission of carbon dioxide increases sharply, accelerating global warming. One of the ways to solve the problem of global warming is to develop alternative energy fuels such as coal and oil. In this context, fuel cells that can be converted from chemical energy to electrical energy have become the focus of world attention. The fuel cell can directly convert chemical energy of the supplied fuel into electric energy with high efficiency through electrochemical reaction, and can continuously obtain electric power with high efficiency through continuous supply of fuel. In a wide range of fuel cells, molten carbonate fuel cell (MCFC) as a large-scale civil power generation device has attracted much attention. It has many advantages, such as a wide variety of fuels, low cost, high power conversion rate and so on. However, there are some defects in the cathode material NiO, which will dissolve slowly with the use of high-temperature molten salt electrolyte for a long time. The metal Ni precipitated on the surface of the cathode and formed a similar bridge structure with the anode material Ni, resulting in short circuit inside the battery.

2. Molten Carbonate Fuel Cell (MCFC)

The electrolyte used in MCFC is the eutectic salt of lithium potassium carbonate or lithium sodium carbonate. As shown in Figure 1, it is mainly composed of metal oxide cathode, metal anode, porous electrolyte membrane, metal polar plate and molten carbonate electrolyte. internal modification can be carried out without expensive metal catalysts such as platinum. the purity requirement for fuel is relatively low. it can support various fuels, especially natural gas, and can obtain higher power generation efficiency.

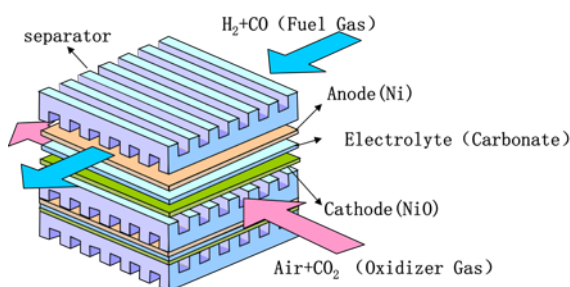


Fig 1. Structure of MCFC.

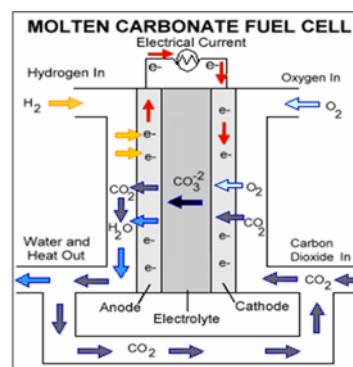
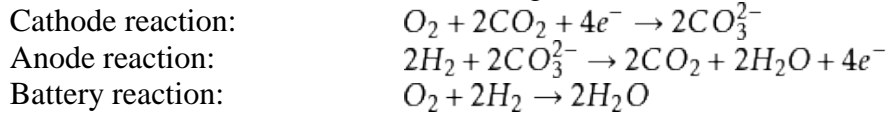


Fig 2. Working Principle of Fuel Cell

2.1. Principles of MCFC

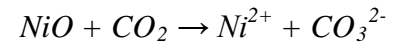
Molten carbonate fuel cells mainly use a material obtained by melting mixed alkaline carbonates such as lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and the like as electrolyte, and use carbonate ions (CO_3^{2-}) as charge carriers. The working principle of molten carbonate fuel cell is shown in Figure 2.



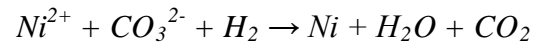
From the above reaction, it can be seen that the conductive ions of mcfc are carbonate ions, CO_2 is the reactant at the cathode and the product is at the anode. In fact, during the battery operation, CO_2 is circulating, that is, CO_2 produced by the anode) Return to the cathode to ensure the continuous operation of the battery. The commonly used method is to exhaust the exhaust gas from the anode chamber through combustion to eliminate H_2 and CO , then separate and remove water, and then return CO_2 to the cathode Recycling, simply speaking, the entire working response of the battery only generates H_2O .

2.2. The problem of mcfc-the cathode material dissolves in the electrolyte

In the cathodic reaction, oxygen and carbon dioxide accept electrons, and a reduction reaction occurs to generate carbonate ions. However, nickel oxide, which is a component of the cathode material, reacts with carbon dioxide side by side, dissolving nickel ions in the electrolyte.



The dissolved nickel ions move into the electrolyte together with the carbonate ions and react with the hydrogen of the anode to precipitate metallic nickel.



After the battery is operated for a long time, NiO particles are dissolved in the molten carbonate, and the active surface area is reduced. At the same time, the precipitated metal nickel causes an internal short circuit between the anode and the cathode, which reduces the battery performance.

3. Research Purpose

As mentioned above, the internal short circuit between the cathode and the anode, which is the problem point of MCFC, greatly reduces the performance of the battery. Therefore, I want to suppress the dissolution of NiO from the cathode to the electrolyte as much as possible. Various studies have been conducted on precipitation-causing short circuits, and the report indicates that the addition of rare earth oxides as the third component to the electrolyte shows a very good effect on reducing the solubility of Ni . This study ① for La_2O_3 After being added to Li/K -based molten carbonate as an electrolyte for fuel cells, the solubility of La was investigated; ② Under the modified electrolyte conditions, the solubility of Ni in the cathode material NiO and the new cathode material LaNiO_3 were investigated. Expedition.

4. Experimental methods

4.1. Experimental setup

Two sets of experimental devices were prepared. The experimental device is shown in Figure 3. Three holes for inlet, outlet, and temperature measurement were opened. The k-type made of a combination of aluminum-nickel wire and chromium-nickel wire was used for temperature measurement. Thermocouple. Insert one side of the thermocouple into a small-diameter alumina protective tube to prevent contact with each other. Put it into a high-purity alumina tube with an inner diameter of 6mm, an outer diameter of 8mm, and a total length of 500mm. Connect a digital multimeter to measure The temperature of the molten salt. The inlet pipe uses a high-purity alumina

tube with an inner diameter of 4mm, an outer diameter of 6mm, and a total length of 500mm. The lower part has an air inlet. The gas introduced into the reaction vessel is controlled by a gas mixer to control the gas. Flow rate: The gas flow rate is measured and adjusted with a flow meter.

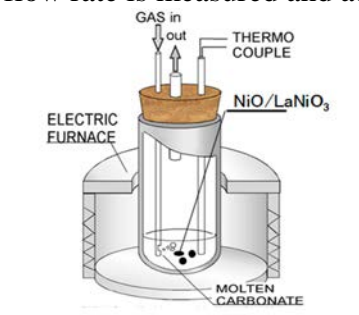


Fig 3. Experimental Device

4.2. Making molten carbonate electrolyte

Since carbonate is deliquescent, in order to avoid moisture in the air, the special reagents Li_2CO_3 and K_2CO_3 manufactured by Wako Pure Chemical Industries, Ltd. are used in an argon drying box.) Mix according to the prescribed molar ratio ($\text{Li/K}=62/38$) to make 150g of electrolyte, put it into a reaction vessel made of high-purity alumina. Place excess La_2O_3 powder in a drying box After vacuum drying at room temperature for 30 minutes, it was placed in a reaction container and heated to 383K at a heating rate of 1K/min in an electric furnace. Vacuum drying was performed at 383K for 30 minutes and vacuum drying at 633K for 12 hours to evaporate water as much as possible. In a carbon dioxide atmosphere, the temperature is raised to 923K at a heating rate of 1K/min to completely melt the carbonate. The carbon dioxide gas maintained at 1atm is flowed into the refined carbonate to react for 24 hours. Li/K molten carbonate electrolyte preparation above Two groups.

4.3. Production of conventional cathode material NiO and new cathode material LaNiO_3

① NiO powder (Wako Pharmaceutical) is made into a sheet with a diameter of 10mm and a thickness of 2mm under high pressure, and sintered in a high-temperature furnace at 800 ° C for 24 hours to make a cathode material. It is crushed into smaller particles with a wooden hammer and put into the first group. Experimental carbonate electrolyte.

② Dissolve quantitative $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pharmaceutical) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pharmaceutical) powder in pure water Then, a tetramethylammonium hydroxide (TMAH) aqueous solution was added to obtain a precipitate. The precipitate was filtered and placed in an oven for 24 hours and dried, and then placed in a 800 ° C high-temperature furnace. After 12 hours of calcination, LaNiO_3 powder was obtained and detected by XRD (Figure 4) .The powder is made into a sheet with a diameter of 10mm and a thickness of 2mm under high pressure, and sintered and set in a high-temperature furnace at 800 ° C for 24h to make a new cathode material. It is broken into smaller particles with a wooden hammer and put into the second group of experiments. Carbonate electrolyte.

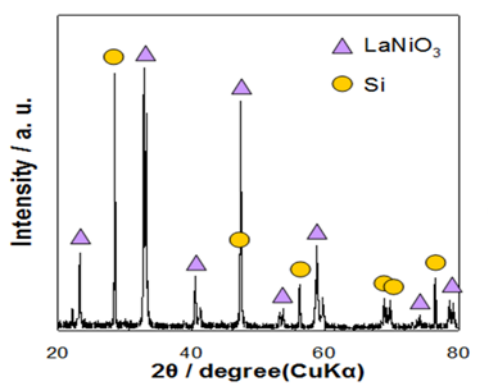


Fig 4. XRD patterns of LaNiO_3 with Si

4.4. Collection of electrolyte samples

Set the temperature of the refined Li/K-based molten carbonate to 923K, and control the oxidant gas CO_2 partial pressure=0.1-0.7atm (O_2 =0.3atm constant, Ar balance), totaling 1atm, total The flow rate is 60ml/min. Samples are taken separately in the two sets of experiments. Before sampling, the alumina tube is lifted above the electrolyte level and left for 30 minutes to prevent suspended $\text{NiO}/\text{LaNiO}_3$ particles from being drawn due to gas flowing in the electrolyte. Come up. When sampling, connect the tail of the alumina tube to the prepared syringe, and take about 0.3g of molten salt electrolyte each time. Drop the sample into an alumina crucible, let it cool and solidify, store it in a sample bottle and weigh it. The sampling operation is basically performed every 12-24h.

4.5. Solubility detection analysis

he solubility test uses an ICP-AES instrument. Before measuring the solubility of Ni in the molten carbonate, confirm that the added La_2O_3 has reached the saturation state. The collected sample is diluted with 4M nitric acid. After the dissolution reaction is visually inspected, Close the lid and use an ultrasonic cleaner to react until the bubbles disappear. Use inductively coupled plasma atomic emission spectrometry (ICP-AES) to detect the solubility of La and Ni elements in the electrolyte.

5. Experimental Results

5.1. Solubility of La in Li/K-based molten carbonate after adding excess La_2O_3

In this two sets of experiments, after adding an excess of La_2O_3 to the Li/K-based molten carbonate electrolyte, the particles of NiO and LaNiO_3 were added to detect the solubility of Ni. Therefore, in Before putting NiO and LaNiO_3 particles, you must first confirm that La_2O_3 is dissolved in the molten carbonate to a saturated state. The La dissolution curve is shown in Figure 5. The horizontal axis represents time, and the vertical axis Represents the molar fraction of $\text{La}_2\text{O}_2\text{CO}_3$ dissolved in Li/K molten carbonate. The solubility of $\text{La}_2\text{O}_2\text{CO}_3$ reaches equilibrium within about 200 hours, depending on The saturation solubility of the amount added under this condition. Under this condition, the saturation solubility is 2.01×10^{-2} . The unit expression is the La content per 1 mol of molten carbonate calculated from the concentration obtained by ICP-AES analysis. Molar fraction of mol.

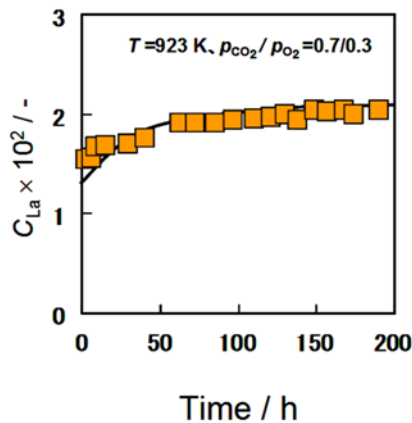


Fig 5. Dependence curves of La_2O_3 in Li/K molten carbonates

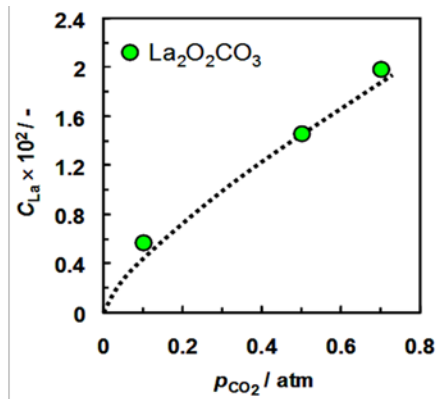


Fig 6. Dependence of a_{La} in molten carbonates on p_{CO_2} at 923K.

5.2. Dependence of La solubility and partial pressure of CO_2

In the experiment, O_2 partial pressure is constant at 0.3atm, Ar is used as balance control, and CO_2 partial pressure is set from 0.1 to 0.7 atm. At 923K, the dependence of the CO_2 partial pressure of $\text{La}_2\text{O}_2\text{CO}_3$ in Li/K molten carbonate is shown in fig. 6, with the horizontal axis representing the CO_2 partial pressure and the vertical axis representing the mole fraction of the solubility of $\text{La}_2\text{O}_2\text{CO}_3$. The saturated solubility of La under each CO_2 partial pressure condition is considered

after it is confirmed that the solubility has not changed for more than 500 hours. The results show that the solubility of La increases with the increase of CO_2 partial pressure.

5.3. Ni solubility of NiO in Li/K based molten carbonate with La_2O_3 added

Li/K based molten carbonate with La_2O_3 added to saturation solubility, NiO at 923K and $\text{CO}_2/\text{O}_2=0.7/0.3\text{atm}$ controlled at a flow rate of 60ml/min The solubility of Ni is shown in Figure 7. The horizontal axis represents time, and the vertical axis represents the mole fraction of Ni dissolved in the Li/K molten carbonate. The moment when 2 g of sintered NiO particles are added to the Li/K-based molten carbonate The horizontal axis is set to 0 hours. The Ni solubility of NiO reaches equilibrium within about 150 hours. Under this condition, the saturated solubility is 19.94×10^{-6} .

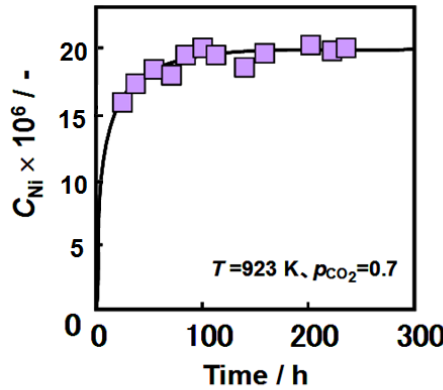


Fig 7. Dependence curves of NiO in Li/K molten carbonates with La_2O_3

5.4. Confirmation of LaNiO_3 test piece

LaNiO_3 was identified using XRD, and the results are shown in Figure 4. The co-precipitation method was used to confirm the formation of LaNiO_3 , and a LaNiO_3 test strip was produced to the same extent as previous studies.

5.5. Ni solubility of LaNiO_3 in Li/K based molten carbonate with La_2O_3 added

Li/K-based molten carbonate with La_2O_3 added to saturation solubility, NiO at 923K and $\text{CO}_2/\text{O}_2=0.7/0.3\text{atm}$ controlled at a flow rate of 60ml/min The solubility of Ni is shown in Figure 8. The horizontal axis represents time, and the vertical axis represents the mole fraction of Ni dissolved in Li/K molten carbonate. 2 g of sintered LaNiO_3 is added to the Li/K molten carbonate. The instant of the particles was set to 0 hours on the horizontal axis. The Ni solubility of LaNiO_3 reached equilibrium within about 150 hours. Under this condition, the saturated solubility was 12.04×10^{-6} .

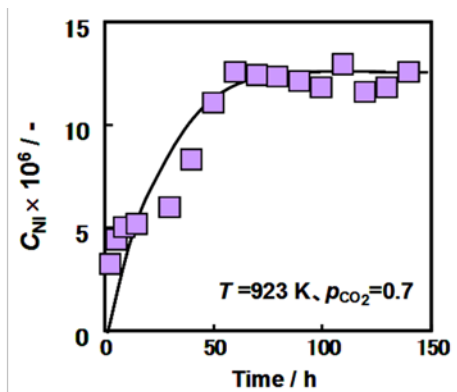


Fig 8. Dependence curves of LaNiO_3 in Li/K molten carbonates with La_2O_3

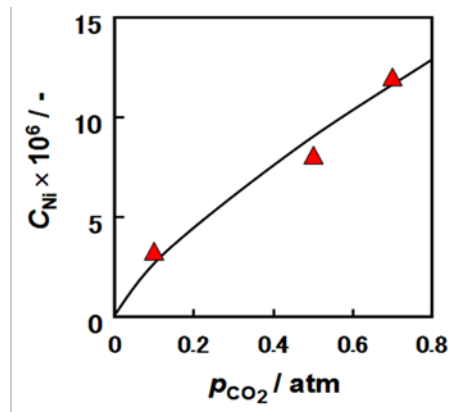


Fig 9. Dependence of Ni solubility in Li/K molten carbonates on p_{CO_2} at 923K.

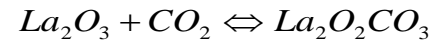
5.6. Dependence of Ni solubility and partial pressure of CO₂

In the experiment, the partial pressure of O₂ is constant at 0.3atm, Ar is used as a balanced control, and the partial pressure of CO₂ is set from 0.1-0.7atm. At the temperature of 923K, La₂O₃ is saturated in Li/K. The dependence of Ni solubility on CO₂ partial pressure of LaNiO₃ in K molten carbonate is shown in Figure 9, with the horizontal axis being the partial pressure of CO₂ and the vertical axis being the molar fraction of Ni solubility. Each CO₂ experiment is carried out under the partial pressure condition for more than 500 hours, and after confirming that there is no change in solubility, it is regarded as the saturated solubility of Ni under this condition. The results show that the solubility of Ni increases with the increase of the partial pressure of CO₂.

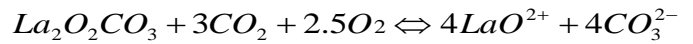
6. Investigation Analysis

6.1. La solubility in Li/K based molten carbonate with La₂O₃ added

La₂O₃ easily absorbs water and carbon dioxide in the air to generate hydroxides and carbonates. Only Li⁺, K⁺, CO₃²⁻ are present in the molten carbonate, and the electrolyte is in CO (TF129) and O₂ introduction atmosphere, the following carbonation reaction occurred.



As shown in Figure 6, by ICP-AES detection, it was found that as the partial pressure of CO₂ increases, the solubility of La₂O₂CO₃ in Li/K-based molten carbonates also increases. With this increase, there is a dependency between the solubility of La and the partial pressure of CO₂. Therefore, we have examined other dissolution equilibrium formulas and consider the following dissolution reaction mechanism:



The active amount of the solid is 1, and there is a large amount of CO₃²⁻ in the molten carbonate, so the active amount is regarded as 1. In addition, because the active amounts of CO₂ and O₂ are under their partial pressures, It can be expressed by P_{CO2} and P_{O2}. So the solubility of La is expressed as follows:

$$C_{La} = K_d \cdot P_{CO_2}^{0.75} P_{O_2}^{0.625}$$

It can be inferred from the above formula that in the Li/K-based molten carbonate saturated with La, there is also a dependence between the solubility of La and the partial pressure of O₂. This experiment has no effect on the partial pressure of O₂. Research will continue as a new topic in the future.

6.2. Ni solubility of LaNiO₃ in Li/K based molten carbonate with La₂O₃ added

At 923K, CO₂/O₂=0.7/0.3atm, the Ni solubility of LaNiO₃ in Li/K based molten carbonate is shown in Figure 10. By adding La₂O (TF156) increases the carbonate ions in the molten carbonate, making it more alkaline, and it is speculated that the solubility of Ni is suppressed. LaNiO (LaNiO (Li) in molten Li/K-based molten carbonate with La₂O₃ added TF159) has a significantly reduced Ni solubility compared to the Ni solubility previously studied, with a solubility of 12.04×10⁻⁶.

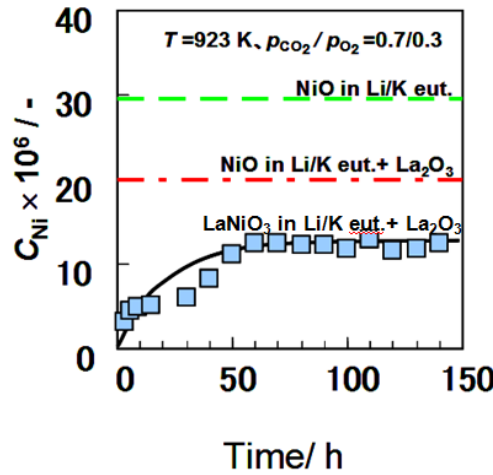
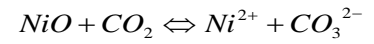


Fig 10. Comparison of Ni Solubility in Li/K Molten Carbonate

6.3. LaNiO₃ Ni solubility CO₂ partial pressure dependence

Previous studies have shown that the solubility of Ni in NiO increases with the partial pressure of CO₂. It can be considered that NiO reacts with CO₂ and dissolves in the electrolyte.



In this formula, let the dissociation constant be k. At this time, k is expressed as:

$$K = \frac{[Ni^{2+}] \cdot [CO_3^{2-}]}{[NiO] \cdot [CO_2]}$$

The active amount of the solid is 1, and there is a large amount of CO₃²⁻ in the molten carbonate, so its active amount is regarded as 1. Since the active amount of CO₂ is under its partial pressure, it can be expressed as P_{CO2}. So the solubility of Ni is expressed as follows:

$$C_{Ni} = K \cdot P_{CO2}$$

If we take the logarithms on both sides of the formula, it is expressed as:

$$\log C_{Ni} = \log K + \log P_{CO2}$$

The logarithm of the partial pressure of CO₂ and the solubility of Ni are taken, and the theoretical slope is 1. The Ni solubility of LaNiO₃ in Li/K-based molten carbonate with La₂O₃ added is the same as above. The logarithmic result of the same method is shown in Figure 11, with a slope of 0.75.

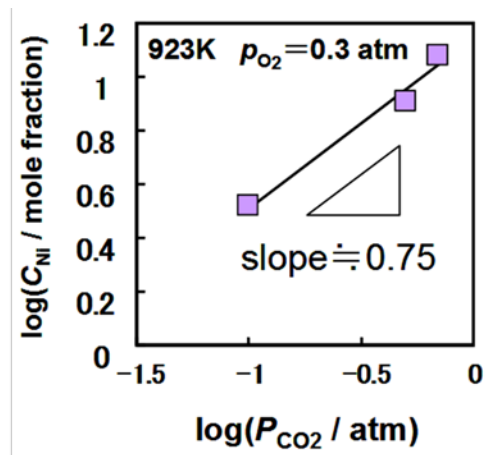
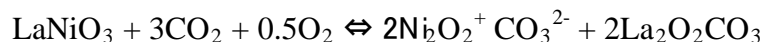


Fig 11. Ni Solubility as a function of p_{CO2} at 923K.

With different CO₂ partial pressure dependence, it can be considered that a dissolution equilibrium different from NiO has occurred. Therefore, it is speculated that the dissolution equilibrium formula of LaNiO₃ can be listed as:



Since the active amounts of CO₂ and O₂ are under their partial pressures, they can be expressed as P_{CO2} and P_{O2}. So the solubility of Ni is expressed as follows:

$$C_{\text{Ni}} = K \cdot P_{\text{CO}_2}^{0.75} \cdot P_{\text{O}_2}^{0.125}$$

According to the above formula, the slope of the dependency of P_{CO2} is 0.75, which is consistent with the experimental results. Since the slope of the dependency of P_{O2} is 0.125, it is speculated that the partial pressure of O₂ has the same dependency. The effect of O₂ partial pressure has not been studied in the experiment, and it can be further explored as a new topic in the future.

7. Conclusion

Through the above experiments, the following conclusions were reached:

① At 923K, standard pressure (CO₂/O₂=0.7/0.3atm), after adding La₂O₃ powder to Li/K series high temperature molten carbonate electrolyte, Ni in NiO The solubility is C_{Ni}=19.94×10⁻⁶. Compared with the previous research, the saturation solubility of Ni has been greatly reduced, which is about 30%.

② LaNiO₃ after adding La₂O₃ powder to Li/K series high temperature molten carbonate electrolyte at 923K, standard pressure (CO₂/O₂=0.7/0.3atm) The solubility of Ni is C_{Ni}=12.04×10⁻⁶. Compared with the previous research, the saturation solubility of Ni is greatly reduced, which is about 60%.

③ It can be seen from Figure 9 that the saturation solubility of Ni increases as the partial pressures of CO₂ increase.

④ La₂O₃ can be added to the electrolyte as a modified substance of molten carbonate.

⑤ LaNiO₃ has a significant decrease in the solubility of Ni in the high-temperature molten salt electrolyte, and has a significant effect in suppressing the internal short circuit of the battery. It can be considered as an alternative material for the cathode material.

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