Preserving nickel electrode conductivity during sintering process using lithium carbonate coatings

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Abstract

The resistance of nickel particles can be decreased by five orders of magnitude when coated with lithium carbonate during sintering in an oxidative atmosphere. The resistance is within a range, in which use is suitable for electrodes in the electroceramic devices. The coated powders have the potential to replace the precious metals (e.g. Pt and Ag) in multilayer electroceramic devices. A systematic study of the influence of sintering atmosphere and temperature on the morphology of Li_2CO_3 -coated Ni particles was investigated via TEM (transmission electron microscopy), SEM-FIB (scanning electron microscopy - focused ion beam) imaging, and TGA (thermogravimetric analysis). The results suggested that the Li_2CO_3 decomposes and produces CO in the presence of residual carbon; CO, as a reducing agent, decreases the amount of NiO phases formed during sintering. At the same time, the NiO phase was doped with Li^+ , resulting in a decrease in its resistivity. The combination of these two processes decreased the resistance of the final Ni electrodes from 140 k Ω to 1 Ω . The effect and role of these two mechanisms were separated, and it is shown that both of them are equally useful in the preservation of electrical conductivity.

Keywords: Nickel; conductivity; lithium; EELS; decomposition; electrode

1. Introduction

Nickel electrodes have been frequently used in electroceramic devices, such as co-fired capacitive devices, multilayer lead free piezoelectrics¹⁻³ and solid oxide fuel cells^{4,5}. To protect Ni from oxidation, a heavily reducing atmosphere e.g. $P_{O_2} = 10^{-10}$ atm should be used⁶. This atmosphere introduces a large number of oxygen vacancies to the system, which reduce the insulation resistance properties and also the life time of devices^{7,8}. In addition, to obtain an atmosphere with an oxygen partial pressure in order of 10^{-10} atm, hydrogen gas should be used as a reducing agent. It was demonstrated that hydrogen can diffuse into electroceramic devices and degrade their insulation properties⁹⁻¹². In order to avoid these shortcomings, one solution is to sinter the devices in less reducing atmosphere, e.g. $P_{O_2} = 10^{-4}$ atm, without using hydrogen and, on the other hand, using some measurements to preserve Ni electrode conductivity. In the previous paper¹³, it was illustrated that the resistance of Ni electrode can be kept as low as 1 Ω by coating Li_2CO_3 around Ni particles after sintering at $P_{O_2} = 10^{-4}$ atm, while the resistance of the uncoated particle was 140 k Ω after sintering under the same conditions. Although the Li_2CO_3 coatings show promising potential in preserving Ni particle conductivity, the mechanism behind the conductivity preservation still needs to be explored.

Two mechanisms were speculated as being responsible for the conductivity preservation in this study. First, the lithium carbonate can decompose in the course of the sintering process and produce CO gas in the presence of carbon^{13,14}. CO gas is a reducing agent and can decrease pO_2 locally. The source of carbon is the organic materials used in making the electrode paste^{15,16}. The second mechanism is to dope the NiO phase in the electrodes with Li^+ in order to increase the Ni^{3+}/Ni^{2+} ratio and encourage electronic polaron hopping between them^{17,18}. Depending on the amount of oxygen, nickel oxide has the possibility of non-stoichiometric defects with Ni vacancies (V''_{Ni})¹⁹⁻²³. V''_{Ni} introduces negative charge to the lattice, which would be compensated by changing the oxidation state of some Ni ions from 2+ to 3+. The mixture of Ni^{3+} and Ni^{2+} enables electron hopping between those ions²⁴. Thus, one can argue that the conductivity of NiO phases can be manipulated by changing the Ni^{3+}/Ni^{2+} ratio through doping. In the

previous work²⁵, it was illustrated that the resistance of Ni foils after a heat treatment in air can be changed from 1 G Ω doped with Al³⁺ to 2 M Ω doped with Zn²⁺. An EELS (electron energy loss spectroscopy) analysis showed that the ratio of Ni³⁺/Ni²⁺ in the Zn²⁺-doped foil is larger than the Al³⁺-doped foil. If this is the case, Li⁺ will be a good candidate to dope the NiO phase, since Li⁺ doping can disturb charge neutrality more and increase the Ni³⁺/Ni²⁺ ratio more effectively. In addition, among the alkali cations, Li⁺ has the closest ionic radius to Ni ions, and it is expected to have the highest diffusion coefficient in NiO crystals. Li⁺ and Ni²⁺ ionic radius are 76 and 69 pm²⁶. In addition, the other authors have reported the decrease in NiO resistivity due to Li⁺ doping^{27,28}.

In the previous paper¹³, a simple and innovative method to coat Li₂CO₃ on Ni particles was introduced, and it was illustrated that the coating is able to effectively preserve Ni electrode conductivity. In this paper, a systematic study on microstructures of Ni electrodes during decomposition and the atom distribution in the Ni electrodes was executed to explore the mechanisms that are responsible for conductivity preservation.

2. Experimental Section

In order to coat Ni particles, the Li₂CO₃ powder was dissolved into deionized water, and then Ni particles were added and stirred to make sure of full wettability of Ni particles. Next, the mixture was heated to evaporate the liquid, while it was mechanically stirred during the entire process. The solution reached saturation, and the chemical compound started to deposit on Ni particles. More detail about the coating process is given in Supporting Information and in the previous paper¹³.

The Li₂CO₃ was bought from Alfa Aesar in powder form, with 99.998 % purity. The Ni powder was the courtesy of JFE Mineral Company and Shoei Chemical, with the average particle size of 300 nm and purity of 99+%. If it did not specify in the text, 17.3 wt% of Li₂CO₃ was used for coating Ni particles.

6 grams of the coated particles were mixed with 1 gram of the 15 wt.% ethyl cellulose solved in dihydro terpineol. The final product was a liquid mixture with a high viscosity, commonly referred to as “electrode ink”. Then the ink was painted on a piece of 1cm by 0.5 cm alumina sheet and dried at 120°C for 20 minutes. After that, the alumina sheets were exposed to different heat treatments at different atmospheres. The heating and cooling rates were 100 °C/min and -50 °C/min, obtained by a homemade fast-heating furnace²⁹. The sintered particles were referred as “sheet” in this paper. The nitrogen and carbon dioxide gases have the purity of 99.999% and 99.99%, respectively. The source of oxygen was the cylinder with 0.1% oxygen balanced with nitrogen.

The electrical resistance measurement was executed by a two-probe method and was explained elsewhere¹³. The SEM (scanning electron microscope) micrographs and TEM (transmission electron microscope) samples were obtained by FEI Helios NanoLab 660 FIB/SEM. The TEM analysis was done by FEI TALOS F200X and TECNAI G20, equipped with EELS (electron energy loss spectroscopy). The TGA (thermogravimetric analysis) tests were done by TA Instrument SDT Q600.

3. Results and discussion

As mentioned earlier, two phenomena of Li_2CO_3 decomposition and Li^+ effect are effective in the conductivity preservation of Ni electrodes. These two phenomena were studied separately, and an effort was made to separate their influences.

3.1 Lithium Carbonate decomposition

Lithium carbonate decomposed into Li_2O and CO_2 around 763°C, based on TGA (thermogravimetric analysis) tests in Supporting Information. Subsequently, CO_2 would be converted to CO in the presence of carbon^{14,30}. The next reaction in low partial pressure of oxygen and the presence of Ni as a catalyst could be the CO decomposition to oxygen and carbon¹³. In Supporting Information, it was demonstrated that the peak of the maximum weight loss in TGA tests due to the decomposition reaction can be

pushed back from 819°C in air to 1086 °C in nitrogen and 1235 °C in carbon dioxide. Also, the results suggest that the decomposition rate of pure Li_2CO_3 powders would be significantly different in CO_2 and nitrogen atmosphere. The effect of sintering atmosphere was discussed in more details in Supporting Information. For instance, applying CO_2 atmosphere during sintering could hinder the first reaction (i.e. producing CO_2 gas) in the chain of the decomposition process; due to the extra CO_2 gas, the reaction would be reluctant to proceed to the right and produce more CO_2 gas, based on Le Chatelier's principle. In other words, Li_2CO_3 can be preserved in CO_2 atmosphere up to 1235 °C. Thus, one may conclude that the Li_2CO_3 decomposition can be manipulated by applying different sintering atmosphere.

The lithium carbonate decomposition was investigated by heating the coated particles to 900 °C and cooling down without holding at five different atmospheres of CO_2 , pure nitrogen, 0.02% oxygen, 0.04% oxygen, and air. The SEM micrographs of the FIB cross section of these sheets are presented in Figure 1. The microstructure of the sheet, exposed to 900 °C in CO_2 , is presented in Figure 1 (a). Based on the discussion above, this micrograph can represent the mixture of Ni and Li_2CO_3 in the early stage of sintering, as if there is no Li_2CO_3 decomposition. As shown in the micrograph, the Li_2CO_3 without decomposition is able to melt and surround all Ni grains; one can consider that as a liquid phase sintering, in which one compound gets melted at the beginning of sintering and surrounds the grains of the second powder^{31,32}. In addition, since there is an unlimited source of CO_2 due to blowing CO_2 gas into the chamber, all the residual carbon would be eliminated by $\text{CO}_{2(g)} + \text{C}_{(s)} \rightarrow 2\text{CO}_{(g)}$ in the early stage of sintering³³.

Figure 1 (b) shows the micrograph of the sheet, sintered under pure nitrogen. There is a thick layer of carbon on the top of the sheet. In the absence of an unlimited source of CO_2 gas and the presence of residual carbon, Li_2CO_3 decomposed to CO. In the next set of reactions, due to the lack of oxygen, CO

decomposed and redeposited carbon on Ni particles at the top of the sheet based on Eq.1³³⁻³⁵. More evidence is provided elsewhere¹³ and also in Figure S4, presented the TEM analyses of the carbon layer.

Eq.1

Now, oxygen would be added to the scenario and increased to 0.02 and 0.04 vol.% and, eventually, air; the microstructure of the sheets is respectfully presented in Figure 1 (c) to (e). The thickness of the carbon layer on the top of the sheets, sintered in nitrogen, 0.02, and 0.04 vol.%, were measured 2.29, 2.0, and 1.6 μm on average, and it disappeared in air. This suggests that the carbon re-deposition decreases by increasing oxygen and, eventually, it becomes zero in air. That observation fits well with the explanation of Eq.1, in which it is suggested that increase in the amount of oxygen drives the equilibrium to the right and prevents carbon re-deposition.

The other observation is that, by increasing the amount of oxygen from pure nitrogen to air, the amount of weight loss increases and as a result, the space between individual Ni grains would increase. The trend of this phenomenon can be traced in Figure 1 (b) to (e). There is a small number of the isolated Ni grains on the top of the cross section in Figure 1 (c); their number increased by increasing the oxygen flow from 0.02 to 0.04% oxygen, and they overcame the entire cross section in air, as shown in Figure 1 (d) and (e). This is due to the fact that the Li_2CO_3 can lose up to 59% of its original weight during the decomposition process. On the other hand, the system can simultaneously compensate some of the weight loss by the carbon re-deposition. Increasing the oxygen flow would hinder the carbon re-deposition process and weight loss would be manifested as the empty space between the grains. To verify this explanation, the amount of Li_2CO_3 decreased from 17.3 wt.% to 3.4 wt.% in the coating process, and the resultant particles heated to 900 °C in air. The cross-section of this sheet is presented in Figure S6. It can be seen that the empty space between grains decreased significantly due to the

decrease in the Li_2CO_3 percentage and, consequently, the weight loss. Furthermore, a similar conclusion can be reached from TGA tests in Supporting Information.

Now, the importance of Figure 1 (a) can be better appreciated. Since CO_2 prevented Li_2CO_3 decomposition and eliminated residual carbon, Figure 1 (a) shows the ideal case of neither the Li_2CO_3 decomposition nor the carbon re-deposition; the Li_2CO_3 coating only melted and enclosed Ni grains. In the mixture of oxygen and nitrogen gas, on the other hand, Li_2CO_3 did the same thing, but it was simultaneously decomposed. However, the decomposition is not necessarily a harmful process, since it produces CO gas and limits the NiO phase formation during the sintering process, as will be discussed in more details later.

Figure 1 The SEM micrographs of FIB cross section of the sheets with 17.3 wt.% of lithium carbonate, heated up to 900 °C at (a) carbon dioxide, (b)nitrogen, (c) 0.02% oxygen (c) 0.04% oxygen, and (d) air.

A detailed study on the Li_2CO_3 decomposition and carbon re-deposition vs. temperature at 0.04% oxygen flow is given in Supporting Information.

3.2 Li^+ effect and distribution

The second mechanism for reducing resistivity is the Li^+ doping effect, as discussed in the introduction. In order to illustrate the Li^+ contribution, two sheets with similar microstructure were selected. The first sheet was made of coated particles and sintered at 1330°C for 3 minutes at 0.04% oxygen, and the other one was made of uncoated particles and sintered in the same program but at 0.02% oxygen. Their microstructures are presented in Figure 2 (a) and (b); there is NiO layer on the top of both sheets, with the minimum thickness of 2.0 and 1.3 μm , respectively. Both sheets have a similar microstructure, in the sense that both have a NiO layer on top. Although the NiO layer is thicker on top of the sheet with Li_2CO_3 , its resistance was measured as 43 Ω , while the resistance of the sheet without Li_2CO_3 was measured as 140k Ω ¹³. A four orders of magnitude decrease in resistance in the sheets with a similar microstructure comes from the Li^+ doping effect. The microstructure of the coated particles were further investigated in the Supporting Information (Figure S2).

Figure 2 SEM micrographs of FIB cross section in the sheets, made of (a) coated particles and sintered in 1330°C for three minutes at 0.04% oxygen (b) uncoated particles and sintered in the same sintering program but at 0.02% oxygen.

The other observation in Figure 2 (a) is that the final microstructure of coated particles is a mixture of Ni and NiO grains with some black islands; that type of microstructure was also noted in the previous paper¹³. Figure 3 shows one of the islands in its matrix together with its EDS (energy dispersive spectroscopy) analysis. As Figure 3 (a) shows, the matrix is made of Ni and NiO grains, and the island is made of a mixture of oxygen, carbon, and lithium and would be called LiCO area. The EDS map of Figure 3 (a) is shown in Supporting Information. The map shows that there is a mixture of Ni and C at the border of the island, suggesting the interdiffusion of the island and the matrix.

Figure 3 (b) shows the LiCO area in a higher magnification, and its EDS maps are presented in Figure 3 (c-e). The EDS analysis suggests that there is not a detectable amount of Ni in LiCO region, and the amounts of oxygen and carbon are not uniformly distributed in the LiCO region. In order to quantitatively show the distribution of carbon and oxygen, an EDS line-scan and the molar ratio of carbon over oxygen, based on EDS data, are presented in Figure 3 (f) and (g), respectively. The line-scan data come from the line, shown in Figure 3 (b) and labeled as 'EDS line scan'. Three regions are detectable: carbon-rich, Li_2CO_3 , and carbon-depleted. These three areas can be located, based on Figure 3 (g), where some areas are above, below, or on the line of 1/3 molar ratio of carbon over oxygen. Since we are certain that the atoms in LiCO region are limited to Li, C, and O (the existence of Li would be demonstrated by EELS later), one can argue that all the plausible solid phases are Li_2O , Li_2CO_3 , and pure

carbon. By considering the cooling rate of $-50\text{ }^{\circ}\text{C}/\text{min}$ in the heat treatments and eutectic reaction at $705\text{ }^{\circ}\text{C}$ in Li_2O and Li_2CO_3 phase diagram³⁶, one can argue that the LiCO area is made up of non-equilibrium phases of Li_2O and Li_2CO_3 , with some rich carbon areas due to the carbon re-deposition.

Figure 3 (a), (b) STEM-Dark Field micrographs of the Ni sheet with 17.3 wt.% Li_2CO_3 sintered in 1330-3 in 0.04% of oxygen flow. The EDS map of (c) carbon, (d) oxygen, and (e) nickel from the area, shown in figure (b). (f) intensity (g) molar ratio of carbon over oxygen vs distance on the line, showed in figure (b). The EELS line scan 1 and 2 are the lines, where EELS analysis in Figure 4 (a) and (c) were done.

The LiCO islands were separated from each other and made a small portion of the microstructure, while the matrix (i.e. the continuous phase) was made of Ni-NiO grains, as shown in Figure 2 (a) and Figure 3 (a). So the most of the electron conductivity happened through the matrix, whose conductivity was determined by Li^+ concentration and $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio.

Two sets of data, Li^+ distribution and $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio, can be provided by EELS analysis. Figure 4 (a) presents the intensity of Li^+ edge vs. distance on the line, labeled as 'EELS line-scan 1' in Figure 3 (a). The intensities suggest that the Li^+ concentration is maximum at the border of the LiCO island and decrease with distance from it. By passing the Ni-NiO grain boundary, the intensity becomes considerably low, indicating Li^+ concentration is negligible in Ni grains. To verify this conclusion, four spectrums of EELS analysis at different points are shown in Figure 4 (b). As discussed in literatures, Li K-edge can be shifted from 54.7 to 61 eV for different Li bonding³⁷⁻³⁹, and Ni has its $\text{M}_{2,3}$ edge at 68 eV³⁷. As can be seen, two edges can be detected at 58.5 and 65 eV in spectrum (1), (2), and (3), which are collected from NiO grain. The place of these points are marked in Figure 4 (a). The spectrum (1) to (3) can be a signature for Ni, Li, and O coexistence. The concentration of Li was related to the intensity of the edge at 58.5 eV. As

illustrated in spectrum (4), Li^+ edge becomes negligible in the Ni grain and the Ni $\text{M}_{2,3}$ edge shift from 65 eV back to 68 eV.

The other set of experiments is core-loss EELS and collecting Ni energy loss at 845 and 874 eV. The ratio of the intensity of the second edge over the intensity of the first edge, shown by R in this paper, is equivalent to the Ni^{3+} concentration over Ni^{2+} concentration^{22,40,41}. So one would be able to trace $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio by EELS analysis, as demonstrated in the previous work²⁵. The significance of $\text{Ni}^{3+}/\text{Ni}^{2+}$ in Ni conductivity was discussed in Introduction and the previous work²⁵.

Figure 4 (c) presents R vs. distance; the EELS data were collected on the line, labeled as 'EELS line-scan 2' in Figure 3 (a). A comparison between Figure 4 (a) and (c) suggests that the ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$ increased by increasing Li^+ concentration except near the island, where Li concentration exponentially increased, while R ratio reached a plateau at 0.45. This upper limit can be justified as the state in which all of the Ni^{2+} ions convert to Ni^{3+} to compensate the charge offset due to Li^+ introduction. On the other hand, there is a lower limit for R, where stoichiometric NiO with minimum Ni^{3+} was tested. The lower limit of R was reported as 0.25 by the authors²⁵ and Muto et al.⁴⁰ As can be seen, every point in the curve of Figure 4 (c) is above the lower limit. One may conclude that Li^+ , even in low concentration, can effectively increase Ni^{3+} in the entire NiO grain. Three typical spectra were selected from the line scan in Figure 4 (c) and are presented in Figure 4 (d). Spectrum (1) is a typical spectrum, which can be found near the LiCO island and since the Ni is diluted by carbon and lithium, its edge intensity is low. By going away from the island, the spectrum evolved to (2) and (3), and the edge intensity increased due to increase of Ni concentration. However, as explained above, we are interested in the R and $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio.

Now, one can have a complete image of the electron conductivity in the sheets. The conductivity occurred through the continuous matrix of Ni and NiO grains. Electrons can easily transfer through Ni

metallic grains, and when they reach the Li doped NiO grains, the electrons can still pass them without much increase in resistivity through the polaron hopping process. This mechanism can justify the decline in the resistance of the sheets, shown in Figure 2, from 140k Ω to 43 Ω .

Figure 4 (a) the intensity of Li edge and (c) the ratio of second edge over the first edge in Ni spectra (shown as R) vs distance along with the image, where the analysis were executed. Typical spectra in line scan of (a) and (c) are shown in (b) and (d) respectively.

3.3 The effect of lithium carbonate decomposition on conductivity preservation

The influence of Li^+ is shown in the previous section specifically by comparing the two cases in Figure 2. It would be informative to repeat the same experiment with and without the effect of Li_2CO_3 decomposition. In order to do so, CO_2 gas was utilized during sintering. As suggested previously, CO_2 can

preserve Li_2CO_3 , and at the same time, burn out all residual carbon. Thus, without the residual carbon, the sintering atmosphere would be CO_2 gas (with a purity of 99.99%) without any reducing agents (i.e., CO). The coated particles were sintered at 1330°C for 3 minutes in CO_2 gas and, afterward, their resistance was measured as $1.2\text{ k}\Omega$, while the resistance of uncoated particles was measured as $80\text{ k}\Omega$. One can argue that this decrease in resistance is only due to the Li^+ -doping effect.

One can argue that the coated particles sintered at CO_2 atmosphere can be compared with the coated particles sintered in 0.02% oxygen balanced with nitrogen. The atmosphere with 0.02% oxygen possessed a higher oxygen content than the CO_2 atmosphere since the CO_2 gas only had a 0.01% impurity comprised of oxidizing agents. In addition, the resistance of uncoated particles, after sintering in the CO_2 and 0.02% oxygen, were measured as 80 and $140\text{ k}\Omega$, respectively. Thus, the 0.02% oxygen atmosphere is more oxidizing than the CO_2 atmosphere.

Next, the coated particles were sintered in the 0.02% oxygen atmosphere, and their resistance was measured as 10Ω . This value is two orders of magnitude less than the $1.2\text{ k}\Omega$ resistance of the CO_2 -sintered sheet. Furthermore, the FIB cross section of the CO_2 -sintered sheet, presented in Figure S5, showed a thick NiO layer of $1.5\text{ }\mu\text{m}$ on the top of the sheet. However, this layer would be negligible in 0.02% oxygen with the average thickness of $0.1\text{ }\mu\text{m}$ as shown in Figure S4 (The effect of the Li_2CO_3 decomposition on NiO layers were further investigated in the previous paper¹³). It can be concluded that although 0.02% oxygen is more oxidizing than the CO_2 atmosphere, the coated particle would have less NiO phase and consequently less resistance due to the decomposition of Li_2CO_3 and the production of CO gas.

4. Conclusions

Coating Ni particles with Li_2CO_3 can preserve the electrical conductivity of the resultant electrode in more oxidative atmospheres during sintering which can offer significant improvements in

electroceramic processing and electrical properties by limiting the concentration of oxygen vacancies. In this study, the underlying mechanisms in the process of conductivity preservation were explored and understood. Two mechanisms of Li^+ doping and Li_2CO_3 decomposition were introduced, and their effects on conductivity preservation were studied independently. It was shown that the Li_2CO_3 melted and flew around the Ni grains; at the same time, it decomposed into CO gas. The CO acted as a reducing agent and could hinder the NiO formation. In addition, a layer of carbon on the sheets was the result of CO gas existence; its thickness was found to be dependent on oxygen percentage and temperature. It was demonstrated that by applying CO_2 gas during the sintering process, the reducing effect of CO gas could be eliminated and, as a result, the resistance increased from 10Ω to $1.2\text{ k}\Omega$ in the same concentration of Li^+ .

The final microstructure of the sheets was a matrix of Ni and NiO grains with islands of residual Li_2CO_3 . The distribution of ions were mapped for this microstructure. The $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio, which controls electron hopping and resistivity reduction in NiO phases was also measured. Two similar microstructures, with and without Li^+ , were selected, and it was shown that the Li doping effect can decrease the resistance from $140\text{ k}\Omega$ to 43Ω .

Both previous observations suggested that the Li^+ doping effect and the production of CO gas were both relevant in preserving the electrical conductivity. The CO gas, as a reducing agent, decreased the amount of NiO phases and hence the oxidation of metallic Ni, while the Li^+ doping decreased the resistance via increasing the $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio. The combination of both mechanisms resulted in a five-orders-of-magnitude decrease in the resistance of the sheets.

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The lithium carbonate coating melts and surrounds Ni particles in early stage of sintering and preserves their electrical conductivity during the sintering in oxidizing atmospheres. The micrograph shows the Ni particles, enclosed with lithium carbonate residues, after sintering.