INFLUENCE OF PREPARATION CONDITIONS ON ELECTRONIC RESISTIVITY OF LiFeO$_2$ SYNTHESIZED IN MOLTEN CARBONATES

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ABSTRACT

LiFeO$_2$ has been synthesized in molten Li$_2$CO$_3$-K$_2$CO$_3$ eutectic at different temperatures and under different gas environments. The electronic resistivity of LiFeO$_2$ was found to be dependent on the partial pressure of CO$_2$ above the carbonate melt. A model for nonstoichiometric LiFeO$_2$ has been proposed to explain these experimental results. Dependence of resistivity on the synthesis temperature was also observed.

INTRODUCTION

The state-of-the-art molten carbonate fuel cell (MCFC) consists of a porous nickel anode (fuel electrode), a porous lithium-doped nickel oxide cathode (oxidant electrode), and a lithium aluminate matrix filled with lithium and potassium carbonates (62-70 mol % lithium carbonate) as the electrolyte. The cell is operated at temperatures of about 923 K and at pressures of 1 to 10 atm, with a humidified mixture of H$_2$ and CO as fuel gas and a mixture of O$_2$ and CO$_2$ containing water vapor as oxidant.

Nickel oxide has been used as the cathode material for MCFCs since 1959 (1). One important problem associated with the NiO cathode is its long-term instability. Nickel oxide dissolves at the cathode and precipitates as metallic nickel in the electrolyte owing to reducing conditions caused by the anode gas. The precipitation of nickel near the anode creates a nickel concentration gradient in the electrolyte which causes further NiO dissolution. This dissolution/precipitation phenomenon limits the life of the NiO; thus, the desired 40,000-h lifetime of the fuel cell for commercial applications will probably not be met under certain operating conditions. Development of alternative cathode materials to NiO has been attempted recently (2,3). In general, any cathode material for MCFCs should have the following characteristics: (i) stability in the fuel cell cathode environment, (ii) adequate electronic conductivity (>0.1 ohm$^{-1}$·cm$^{-1}$ at 923 K), (iii) low solubility in the electrolyte and no precipitation in the anode environment, and (iv) good catalytic activity for cathode reactions. LiFeO$_2$ is chemically stable, has low solubility, and does not precipitate in the anode environment (2,3). However, the resistivity of the material (in undoped form) under cathode conditions needs to be lowered before it can be used as electrode material.
There are few studies (4-9) reported in the literature on the structure and properties of LiFeO₂. The resistivity of LiFeO₂ prepared from Fe₂O₃ and Li₂CO₃ at 1023 K in air was investigated by Fayard (6). Fayard (6) reported that nonstoichiometric LiFeO₂ with lithium excess was formed by reaction of Fe₂O₃ with excess Li₂CO₃. In the present work, the influence of preparation conditions on the electronic resistivity of LiFeO₂ synthesized in molten Li₂CO₃-K₂CO₃ was investigated. The experimental results are presented and discussed.

EXPERIMENTAL

Samples of undoped LiFeO₂ were prepared by reacting Fe₂O₃ with Li₂CO₃ in excess Li₂CO₃-K₂CO₃ eutectic (62 mol % Li₂CO₃) for 60 h at several temperatures and under different gas atmospheres. After reaction, the products were washed with distilled water to remove the excess carbonate; they were then dried and pressed into pellets (about 2.85 cm diameter, 0.2 cm thick). The pellets were sintered in the synthesis gas (with the single exception described later) at 1323 K for 1 h. The electronic resistivity of the pellet was determined by the DC technique of van der Pauw (10). The materials were also characterized by X-ray diffraction, absorption spectrophotometry, chemical analysis, and Seebeck coefficient measurements. Chemical analysis for Fe⁴⁺ in LiFeO₂ was carried out by dissolution of LiFeO₂ in an excess of reducing material (As₂O₃) under a nitrogen atmosphere followed by titration of the remaining reductant with standard ceric sulphate solution.

RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature dependence of the electronic resistivity of LiFeO₂ synthesized at 973 K in molten Li₂CO₃-K₂CO₃ under different mixtures of O₂ + CO₂ + N₂. No effect on resistivity could be detected for oxygen partial pressure of 0.15-0.7 atm and for partial pressure of CO₂ > 0.005 atm. Under these conditions, the resistivity of LiFeO₂ was about 300 ohm·cm at 923 K. On the other hand, Fig. 1 shows that synthesis with partial pressure of CO₂ < 0.005 atm produced LiFeO₂ with lower resistivity and that the resistivity decreased with decreasing CO₂ partial pressure. LiFeO₂ synthesized under air (partial pressure of CO₂ = 0.0003 atm) had a resistivity of 2-5 ohm·cm at 923 K.

The partial pressure of CO₂ will affect the activity of lithium oxide in the carbonate melt, and in that way, can affect the cation ratio (Li/Fe) of the lithium iron oxide synthesized in the melt. This effect is discussed by Schmalzried (11) and Smyth (12,13) for general ternary oxides. These authors point out that complete thermodynamic definition of a ternary oxide requires the specification of three variables (temperature, partial pressure of oxygen, and either binary...
oxide activity or ratio of the two cationic species). In the syntheses of LiFeO$_2$ in Li$_2$CO$_3$-K$_2$CO$_3$ eutectic, the activity of lithium oxide is determined by the gas composition, especially partial pressure of CO$_2$. Low partial pressure of CO$_2$ enhances the activity of lithium oxide, which tends to result in a more lithium-rich compound, i.e., a LiFeO$_2$ compound with a Li/Fe ratio > 1. The following possibilities of Li/Fe nonstoichiometry are recognized: (i) Li$_{1+x}$Fe$_{1-x}$O$_2$, LiFe$_{1.8}$O$_2$, and Li$_{1.5}$FeO$_2$. The model Li$_{1+x}$Fe$_{1-x}$O$_2$ was proposed by Fayard (6) and Anderson and Schieber (8) as the composition for nonstoichiometric LiFeO$_2$ prepared from Fe$_3$O$_4$ and Li$_2$CO$_3$ in air. It should be noted that while it is probable that the material has excess-oxygen nonstoichiometry, the discussion here will be focused on the effect of partial pressure of CO$_2$ and the consequent effect on resistivity via altering the Li/Fe cation ratio.

The activation energy of conduction of LiFeO$_2$ prepared in air is typically 0.4 eV, indicating a probable hopping mechanism. In this case, iron must exist in two valence states. In the first two defect structures given above for LiFeO$_2$, synthesized in low partial pressure of CO$_2$, the conductivity is due to the mixed valence states of Fe$^{3+}$ and Fe$^{4+}$ (p-type conduction); in the third structure, the mixed valences are Fe$^{3+}$ and Fe$^{2+}$ (n-type conduction). Chemical analysis of air-prepared LiFeO$_2$ indicates the presence of Fe$^{3+}$ as the minor species. This result suggests that the nonstoichiometric composition of LiFeO$_2$ prepared under low CO$_2$ partial pressures is either Li$_{1+x}$Fe$_{1-x}$O$_2$ or LiFe$_{1.8}$O$_2$. Seebeck measurements on air-prepared samples, performed by H. Anderson of the University of Missouri-Rolla, show positive Seebeck coefficient (Fig. 3), indicating p-type conduction. While Fe$^{4+}$ cannot presently be detected by absorption spectrophotometry, the method does indicate the absence of Fe$^{2+}$ in those samples.

The presence of Fe$^{4+}$ in LiFeO$_2$ synthesized under low partial pressure of CO$_2$ is consistent with the results of an experiment which studied the variation of the resistivity of air-prepared LiFeO$_2$ with cover gas. A plot of the resistivity versus time and cover gas for an air-prepared LiFeO$_2$ sample is given in Fig. 4. The improvement in conductivity under an oxygen atmosphere also indicates that conductivity is due to the presence of Fe$^{4+}$. If the conductivity were due to Fe$^{3+}$, increased partial pressure of oxygen would not be expected to improve the material conductivity. In addition, Fig. 4 shows a wide variation of equilibration times for different gases. This may be indicative of the relative defect concentration in the presence of the various gases.

A test was carried out to examine the proposed nonstoichiometric model for LiFeO$_2$. Figure 5 shows the resistivity of a LiFeO$_2$ sample synthesized under air and then sintered under high CO$_2$ partial pressure (0.3 atm). The data in Fig. 5 are consistent with the proposed model and can be explained as follows. The LiFeO$_2$ synthesized under air is a nonstoichiometric compound of the type Li$_{1+x}$Fe$_{1-x}$O$_2$ (or LiFe$_{1.8}$O$_2$). When the material is sintered under 30% CO$_2$-70% air, it tends toward a stoichiometric Li/Fe ratio:

599
\[ \text{Li}_{1+x}\text{Fe}_{1-x}\text{O}_2 = (1-x)\text{LiFeO}_2 + x\text{Li}_2\text{O} + x/2\text{O}_2 \]  

[1]

\[ \text{Li}_2\text{O} + \text{CO}_2 = \text{Li}_2\text{CO}_3 \]  

[2]

Because of this, the resistivity of the material is high in the lower temperature range of Fig. 5. However, because the resistivity measurements were carried out under air (partial pressure of CO\(_2\) = 0.0003 atm), the reactions [1] and [2] are reversed, making the material nonstoichiometric at higher temperatures. Lower resistivity is thus observed. The resistivity of LiFeO\(_2\) synthesized in high partial pressure of CO\(_2\) is, on the other hand, not changed when measured in air; because resistivity measurements are carried out without the presence of Li\(_2\)CO\(_3\), no lithium is available for incorporation to alter the Li/Fe ratio.

Although not enough information is available at present to determine whether the nonstoichiometric LiFeO\(_2\) is Li\(_{1+x}\)Fe\(_{1-x}\)O\(_2\) or LiFe\(_{1-x}\)O\(_2\), the composition Li\(_{1+x}\)Fe\(_{1-x}\)O\(_2\) appears to be more probable. The stoichiometric LiFeO\(_2\) at 973 K has a disordered cubic structure, with lithium and iron distributed randomly on a single set of lattice sites. The composition LiFe\(_{1-x}\)O\(_2\) is a representation of an iron vacancy. In the presence of excess Li\(_2\)CO\(_3\) during synthesis, it is unlikely that the iron sites would remain vacant.

LiFeO\(_2\) has also been synthesized in air at different temperatures. The resistivity of LiFeO\(_2\) synthesized at 903-973 K decreases with increasing synthesis temperature (Fig. 6). For example, the resistivity at 923 K of LiFeO\(_2\) synthesized at 903 K is about 120 ohm-cm, compared with about 72 ohm-cm for 923 K synthesis and about 3 ohm-cm for 973 K synthesis. At present, the type of nonstoichiometry (oxygen nonstoichiometry or Li/Fe nonstoichiometry) responsible for this phenomenon has not been investigated.

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Fig. 1. Resistivities of LiFeO$_2$ Synthesized at 973 K under Different Partial Pressures of CO$_2$

Fig. 2. Resistivity of LiFeO$_2$ Synthesized at 973 K under Different Partial Pressures of O$_2$

Fig. 3. Seebeck Coefficient of LiFeO$_2$ Synthesized at 973 K in Air
Fig. 4. Resistivity of LiFeO₂ Synthesized in Air as a Function of Time and Cover Gas

Fig. 5. Resistivity of LiFeO₂ Synthesized and Sintered under Different Gas Mixtures

Fig. 6. Resistivity of LiFeO₂ Synthesized in Air at Different Temperatures