

Mg_xFe_{3-xx}O_{4±δ} Spinels as Potential Consumable Anodes for Pyroelectrolysis

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Solid solutions with monoxide Mg_{1-x}Fe_xO_{1+d} or spinel structure Mg_{1-x}Fe_{2+x}O_{4±d} were prepared under suitable reducing conditions and their electrical properties were characterized by suitable methods. The concentration of charge carriers was estimated from Seebeck coefficient measurements and compared with oxygen stoichiometry changes, which were used to evaluate changes in Fe²⁺:Fe³⁺. Electrical measurements were also used to monitor phase changes on thermal cycling or on varying the oxygen partial pressure. The thermal expansion was measured to assess the stability to thermal cycling and its dependence on composition. The flexural strength was also measured. Computer modelling combined was used for structural analysis of the effects of composition and working conditions on structure, including the occupancy of octahedral and tetrahedral sites and lattice parameters. The consistency of computer modelling was confirmed by agreement with structural refinement of XRD data and measured properties such as thermal expansion. Computer modelling was also used to predict diffusion coefficients.

Introduction

Though Fe oxide phases (magnetite and wustite) possess sufficiently high conductivity to be considered as potential consumable anodes for pyroelectrolysis, their redox changes imply stability limitations. Their refractoriness is also insufficient for application at very high temperatures. Thus, one considered other materials with similar structure types such as spinels Mg_{1-x}Fe_xO₄. The phase diagram predicts significantly wide composition ranges in air, and above the melting temperature of Fe [1].

Preparation

Since composition ranges of spinel phase become narrower on cooling, one studied suitable conditions for the synthesis of these materials, and their sintering. The requirements of controlled atmospheres to perform the synthesis were confirmed experimentally. Note that conditions of powder synthesis may determine the ability to obtain single phase materials (Figure 1). Partial decomposition of the main phase may also impair high temperature electrical properties of Mg_{1-x}Fe_{2+x}O₄ spinels.

Transport properties and defect chemistry

Phase changes may affect the conductivity [2], except possibly at very high temperatures, when one expects single phase spinels. Relevant results are shown in Figure 2. Measurements for pure magnetite were performed in inert Ar atmosphere to prevent oxidation to hematite. T-dependence is rather complex at lower temperatures, including changes in activation energy, probably due to gradual phase change.

Seebeck coefficient measurements suggest important differences between the dependence of charge carrier concentrations in Mg_{0.7}Fe_{2.3}O₄ and spinels with smaller deviations from nominal molar ratio Fe:Mg=2:1 (Figure 3). The negative value of Seebeck coefficient indicates that the electronic conduction in these materials is n-type, and the actual values allowed one to estimate the concentration of charge carriers.

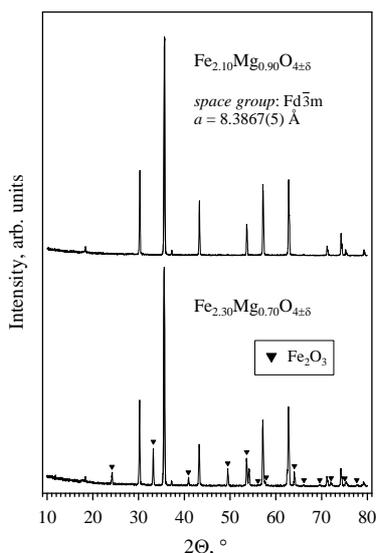


Figure 1. XRD of Mg_{1-x}Fe_xO₄ samples prepared by calcination in air at 1400°C and sintering at 1550°C in Ar

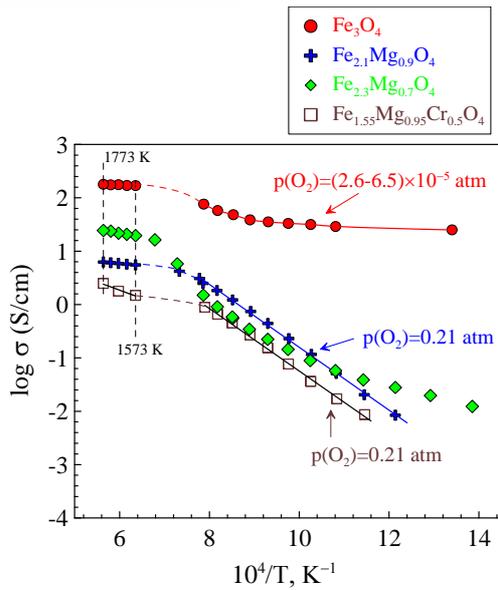


Figure 2. Electrical conductivity at high temperatures

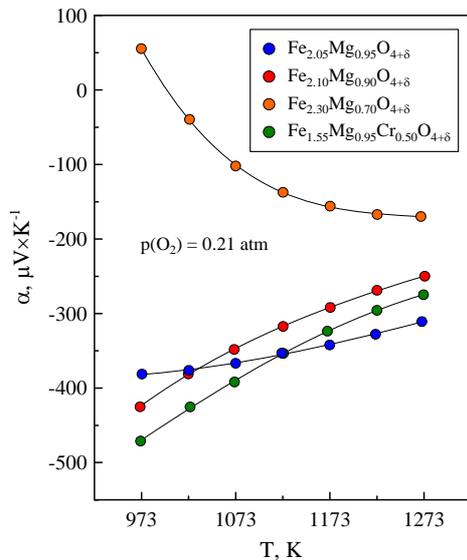


Figure 3. Seebeck coefficient of spinel phases at intermediate temperatures

These materials may undergo significant changes in oxygen stoichiometry [3], which may be related to charge carrier concentrations. Oxygen stoichiometry changes were evaluated from TG results (Figure 4) and the absolute value of oxygen stoichiometry was measured by complete reduction to metallic Fe and MgO. Decrease of oxygen stoichiometry with increasing temperature indicates increasing concentration of charge carriers, as given by Seebeck coefficient measurements. Indeed, oxygen stoichiometry also drops under reducing conditions, yielding higher concentration of charge carriers, and increase in conductivity.

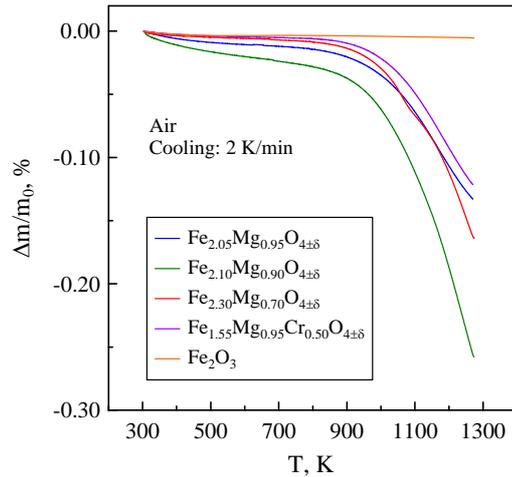


Figure 4. TG showing T-dependent O stoichiometry

Thermomechanical Testing

The thermal expansion coefficient (Table I) is higher for lower contents of Mg, showing that these materials run higher risks associated with thermal shock.

Table I. Flexural strength of spinel-based ceramics

Composition	Atm.	Strength MPa	
		300 K	1173 K
Fe ₃ O ₄	Árgon	-	89
Fe _{2.05} Mg _{0.95} O ₄	Air	194	106
Fe _{2.30} Mg _{0.70} O ₄	Air	247	122

Table II. Thermal expansion coefficient

Composition	T, K	$\alpha \times 10^6, K^{-1}$
Fe _{2.10} Mg _{0.90} O _{4±δ}	300-580	9.80
	580-1050	14.3
	1050-1370	16.1
Fe _{2.30} Mg _{0.70} O _{4±δ}	300-580	9.96
	580-900	13.3
	900-1200	14.6
	1200-1370	26.7
Fe _{1.55} Mg _{0.95} Cr _{0.50} O _{4±δ}	300-500	9.56
	500-800	9.63
	800-1370	13.2

A 3-point bending method using an Instron-1185 instrument equipped with sealed thermo-chamber was used to measure mechanical strength (Table II). These results show that the mechanical strength of

spinel increases with the contents in Mg, i.e., opposite to the trend observed for increase in electrical conductivity. Co-existence of phases or gradual phase change in $\text{Fe}_{2.30}\text{Mg}_{0.70}\text{O}_4$ may explain its poorer mechanical strength. In extreme cases of severe reduction or oxidation these samples broke into pieces, as found on attempting to estimate chemical diffusivity by a cycle of reduction and re-oxidation.

Modelling of structure and properties

Computer modelling was used to obtain insight into the structure and properties of these materials. Calculations were computed with GULP and DL POLY softwares, based on $4 \times 4 \times 4$ supercell (~3600 atoms). Expected point defects were used to model changes in oxygen stoichiometry and $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio vs T and P_{O_2} . The distribution of Fe^{2+} , Fe^{3+} and Mg^{2+} ions in octahedral and tetrahedral positions were also modelled. Energy calculations show that site inversion is unfavourable, which is consistent with Rietveld refinement of XRD (Figure 5). For $\text{Mg}_{0.95}\text{Fe}_{2.05}\text{O}_4$ one predicted 0.08 Mg and 0.92 Fe in tetrahedral positions. Octahedral positions are filled with 0.87 Mg and 1.13 Fe. One also predicted that addition of Cr lower the energy of inversion, yielding larger fractions of Mg in tetrahedral sites. Again, Rietveld refinements of $\text{Mg}_{0.95}\text{Fe}_{1.55}\text{Cr}_{0.5}\text{O}_4$ data indicate 0.23 Mg, 0.04 Cr and 0.73 Fe in tetrahedral positions. Note that high occupancy of Fe in octahedral positions is likely to be more favourable for electrical conduction.

Simulations also allow predictions of thermal expansion, based on the slope at temperatures below melting; this is consistent with the experimental data (Table II), and the discontinuity is consistent with the actual melting temperature. Lattice simulation also yielded predictions of diffusion coefficients for different species, and their activation energy. The results show that the diffusion coefficients of cations are in the same order of those obtained for oxygen diffusion, at least in the vicinity of melting temperature.

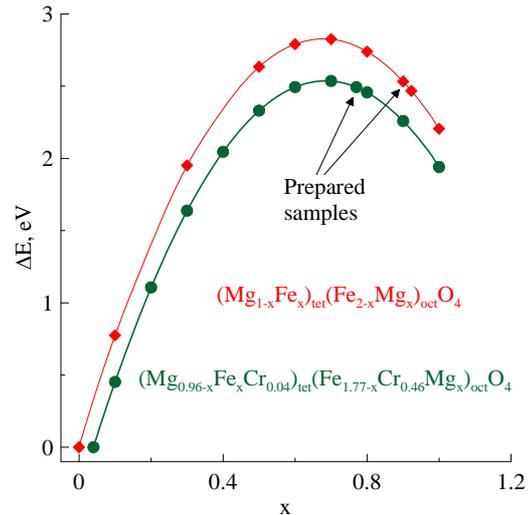


Figure 5. Spinel inversion energy per formula unit, calculated using GULP software

Conclusion

$\text{Mg}_{1-x}\text{Fe}_x\text{O}_4$ spinels have been prepared and characterized as potential consumable materials for pyroelectrolysis. Though the conductivity is still lower than for magnetite, one attained promising results and guidelines for understanding structure property relations. These can be used to attain further improvements. The thermomechanical properties were also characterized. Computer simulations were used to confirm structural features and to predict relevant high temperature properties which are difficult to measure.

Acknowledgements

The present work is part of the ULCOS program, which operates with direct financing from its 48 partners, especially of its core members (Arcelor-Mittal, Corus, TKS, Riva, Voestalpine, LKAB, Saarstahl, Dillinger Hütte, SSAB, Ruukki and Statoil), and has received grants from the European Commission under the 6th Framework RTD program and the RFCS program¹.

References

- [1] I.H.Jung, S.A.Decterov, A.D.Pelton, J. Phys. Chem. Solids, 65 (2004) 1683
- [2] S.H.Kang, S.H.Chang, H.I. Yoo, J.Solid State Chem., 149 (2000) 33
- [3] S.H.Kang, H.I.Yoo, J. Solid State Chem., 139 (1998) 128

¹ Priority 3 of the 6th Framework Programme in the area of "Very low CO₂ Steel Processes", in co-ordination with the 2003 and 2004 calls of the Research Fund for Coal and Steel