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Redox stability and high-temperature electrical conductivity of magnesium- and aluminium-substituted magnetite

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Abstract

Spinel-type magnetite-based oxides, possessing relatively high electrical conductivity, are considered as promising consumable anode materials for high temperature pyroelectrolysis, a breakthrough low-CO_2 steel technology to overcome the environmental impact of classical extractive metallurgy. The present work was focused on the analysis of phase stability, thermal expansion and high-temperature electrical conductivity in $(Fe,Mg,Al)_3O_4$ system under oxidizing and mildly reducing conditions. Metastable, nearly single-phase at room temperature $(Fe,Mg,Al)_3O_4$ ceramics was obtained by sintering at 1753–1773 K for 10 h in argon atmosphere. Thermal expansion and redox induced dimensional changes were studied on heating, using TG, XRD and dilatometry. The results revealed that magnesium improves the tolerance against oxidative decomposition and minimizes unfavorable dimensional changes in ceramic samples upon thermal cycling. Co-substitution of iron with aluminium and magnesium was proved to be a promising strategy for improvement of refractoriness and phase stability of Fe_3O_4-based spinels at elevated temperatures, without significant reduction in the electrical conductivity.

Keywords: Electrical conductivity; Thermal expansion; Spinel; Redox stability; Magnetite

1. Introduction

Steel production by molten oxide electrolysis promises environmental advantages over classic extractive metallurgy, by eliminating CO_2 emissions and reducing energy consumption.[1–3] Though theoretical simulations and predictions for the process are very optimistic,[1] this concept is still far from being convincingly demonstrated even at laboratory scale. The inherent difficulties are largely associated with highly corrosive nature of high-temperature molten electrolytes, and finding suitable anode materials. In particular, noble metals (e.g., Ir) were proposed for small scale demonstration,[3] but they are still far from being truly inert in molten oxide electrodes, while their cost is not affordable for mass production. Similarly, although Mo showed good prospects for electric boosting in glass technology, one cannot consider anodic polarization of Mo electrodes in contact with molten oxide electrolytes. Thus, a major challenge is to seek alternative concepts of consumable electrodes, as currently used in aluminium production by electrolysis of melts.

Pure magnetite, Fe_3O_4, is known to show relatively good refractoriness and high temperature electronic conductivity.[4–8] It has been considered as a prospective candidate for consumable anodes in high temperature pyroelectrolysis,[1,9] due to its compatibility with relevant molten oxide systems (e.g., SiO_2–MgO–FeO_x) and affordable cost for mass production. An important advantage of magnetite also includes chemical composition itself, which does not lead to contamination of the system and may even account for a fraction of iron oxide raw materials. However, magnetite is thermodynamically unstable in air below 1667 K and even in inert gas ($p(O_2) \approx 10$ Pa) below 1300–1373 K.[10] Anodic polarization during electrolysis may also promote oxidation of magnetite to hematite, requiring

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higher operation temperatures to retain electrochemical stability of the magnetite phase, and, thus, sufficient refractoriness. Redox stability of magnetite can be improved by substitution of iron with redox stable oxides, and, for that matter, magnesium and aluminium oxides look very attractive due to their low costs. Moreover, these oxides are also among the most important components of refractory materials for high temperature molten systems. As an example, substitution of iron with Al^{3+} or Mg^{2+} is known to shift the melting points from 1811 K for Fe_3O_4 to 2013 K for $FeAl_2O_4$ and 2023 K for $MgFe_2O_4$, i.e., well above the melting point of iron (1808 K) and the temperature range proposed for iron or steel production from iron ore by pyroelectrolysis. However, redox stability requirements are often in trade-off relation with electrical conductivity. In particular, although the phase diagrams[11,12] predict substantially large compositional ranges for stable $Fe_{3-x}Mg_xO_4$ spinels even in contact with pure oxygen atmosphere, partial iron substitution with magnesium significantly decreases the electrical conductivity at 1250–1773 K.[8] On the contrary, partial substitution with aluminium in magnetite has weaker negative impact on the conductivity but leads to a decrease in the redox stability.[13] Thus, a promising strategy may comprise co-substitution of magnetite with Mg and Al in the concentration range where aluminium may provide just an improvement of refractoriness without significant deterioration of the electric properties, whilst magnesium is expected to enhance the tolerance against oxidative decomposition. Earlier works on this ternary system[14–17] were mostly based on high magnesia or alumina contents and failed to attain the level of electrical conductivity, required for feasible consumable anodes in pyroelectrolysis. In addition, to our best knowledge, no systematic studies of the high-temperature redox stability for these materials were yet performed.

Thus, the present work focuses on studies of phase relationships, redox stability and high-temperature electrical conductivity in the $(Fe,Al,Mg)_3O_4$ system under oxidizing and mildly reducing conditions. The selection of compositions was carried out assuming reasonably high electrical conductivity by extending the composition-property relations previously reported for binary systems $Fe_{3-x-y}Mg_xCr_yO_4$[8] and $Fe_{3-z}Al_zO_4$.[13] Particular attention is also given to the relevant properties in the intermediate temperature range, aiming on guidelines for electrode integrity, which may depend largely on the operation regime of the electrolysis cell.

2. Experimental

The powders of $Fe_{2.6}Al_{0.2}Mg_{0.2}O_4$, $Fe_{2.3}Al_{0.2}Mg_{0.5}O_4$, $Fe_{2.2}Al_{0.1}Mg_{0.7}O_4$, $Fe_{2.1}Al_{0.2}Mg_{0.7}O_4$ (further referred as moderately substituted), $Fe_{1.55}Al_{0.5}Mg_{0.95}O_4$ and $Fe_{1.55}Al_{0.95}Mg_{0.5}O_4$ (highly substituted) were prepared by solid state route from stoichiometric amounts of $FeC_2O_4 \cdot 2H_2O$ (99%, Sigma–Aldrich), Al_2O_3 (10 μm, 99.7%, Sigma–Aldrich) and $Mg(NO_3)_2 \cdot 6H_2O$ (99%, Avocado Research Chemicals). Solid state synthesis was performed in air at 1173–1473 for 15–20 h, with multiple intermediate grindings. After subsequent ball-milling of thus prepared powders with ethanol, disk-shaped ceramic samples were compacted uniaxially at 300–400 MPa, sintered at 1753–1773 K for 10 h in argon atmosphere ($p(O_2) \sim 10^{-5}$–10^{-4} atm) and cooled down to room temperature at 3 K/min. Hereafter, thus prepared ceramics are referred to as "as-prepared" samples. Identical thermal cycle was used to prepare the ceramic samples in air atmosphere. For X-ray diffraction (XRD) and thermogravimetry (TG) studies, the ceramics were ground to powders in a mortar. For the measurements of total conductivity and thermal expansion, the obtained disk samples were cut into rectangular bars (∼2 mm × 3 mm × 12 mm). After polishing, experimental density of the ceramics was measured by Archimedes method.

X-ray diffraction patterns were recorded using a Rigaku D/Max-B diffractometer (Cu Kα, $2\Theta = 10$–$80°$, step 0.02°, exposition 2 s). Unit cell parameters were calculated from the diffraction data using profile matching method in Fullprof software.[18] High-temperature XRD analysis was made on Philips X'pert MPD equipment in vacuum ($\sim 10^{-7}$ atm). For SEM/EDS analysis (Hitachi SU-70 model equipped with Brucker silicon drift EDS detector), selected ceramic samples were polished and annealed at 1673 K (0.5 h) in Ar. TG studies (Setaram SetSys 16/18 instrument, sensitivity 0.4 μg, initial sample weight ∼0.5 g) were performed in a flow of argon or dry air at 298–1373 K with constant heating/cooling rate of 2 K/min. Each TG procedure was repeated under identical conditions (temperature program and atmosphere) using a reference alumina sample and the obtained baseline was subtracted from experimental data in order to correct for buoyancy effects.

Thermal expansion of $(Fe,Al,Mg)_3O_4$ ceramics was measured on heating (3 K/min) up to 1350 K in argon and air atmospheres, using a vertical alumina dilatometer Linseis L75V/1250 with a gas system, including an yttria-stabilized zirconia (YSZ) oxygen sensor at the outlet. Total electrical conductivity (σ) was measured by 4-probe DC technique at 750–1773 K in the oxygen partial pressure $p(O_2)$ range from 10^{-5} to 0.21 atm in flowing air–Ar mixtures. The $p(O_2)$ in the gas flow was monitored using an YSZ oxygen sensor.

Static lattice simulations were performed using GULP software[19,20] in the way, similar to that previously described for $(Fe,Al)_3O_4$ spinels.[13] Simulations were based on 1004 supercells (2 × 2 × 2) with random distribution of cations in tetragonal and octahedral sublattices, including previously reported results for pure magnetite and $(Fe,Al)_3O_4$.[13] The interatomic potentials, used for simulation, are given in Table 1. The collected data of the lattice energy (in GULP formalism) E_{cell} were firstly fitted vs. total magnesium content $[Mg^{2+}]$ and amounts of Mg^{2+} and Fe^{2+} in octahedral sites, $[Mg_O^{2+}]$ and $[Fe_O^{2+}]$, correspondingly, using formal linear regression model:

$$E_{cell} = E_0 + a_{Mg}[Mg^{2+}] + b_{Mg}[Mg_O^{2+}] + b_{Fe}[Fe_o^{2+}] \qquad (1)$$

where E_0 corresponds to the lattice energy for undoped and not inverted magnetite, a_{Mg} is an impact of the substitution with Mg, b_{Mg} is an impact of magnesium in octahedral positions, and b_{Fe} is an impact of the spinel inversion (i.e., Fe^{2+} in octahedrally coordinated sites). Similar modelling was then performed for the ternary $(Fe,Al,Mg)_3O_4$ system, with introduction of the