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High-temperature conductivity, stability and redox properties of $Fe_{3-x}Al_xO_4$ spinel-type materials

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Abstract

Iron-based oxides are considered as promising consumable anode materials for high temperature pyroelectrolysis. Phase relationships, redox stability and electrical conductivity of $Fe_{3-x}Al_xO_4$ spinels were studied at 300–1773 K and $p(O_2)$ from 10^{-5} to 0.21 atm. Thermogravimetry/XRD analysis revealed metastability of the sintered ceramics at 300–1300 K. Low tolerance against oxidation leads to dimensional changes of ceramics upon thermal cycling. Activation energies of the total conductivity corresponded to the range of 16–26 kJ/mol at 1450–1773 K in Ar atmosphere. At 1573–1773 K and $p(O_2)$ ranging from 10^{-5} to 0.03 atm, the total conductivity of $Fe_{3-x}Al_xO_4$ is nearly independent of the oxygen partial pressure. The conductivity values of $Fe_{3-x}Al_xO_4$ ($0.1 \leq x \leq 0.4$) at 1773 K and $p(O_2) \sim 10^{-5}$ to 10^{-4} atm were found to be only 1.1–1.5 times lower than for Fe_3O_4, showing high potential of moderate aluminium additions as a strategy for improvement of refractoriness for magnetite without significant deterioration of electronic transport.

Keywords: Electrical conductivity; Thermal expansion; Spinels; Redox stability

1. Introduction

Molten oxide electrolysis was recently proposed as a breakthrough low-CO_2 steel technology to overcome the environmental impact of classical extractive metallurgy.[1,2] Yet, this concept is still far from being convincingly demonstrated even at laboratory scale, largely due to the highly corrosive nature of high-temperature molten electrolytes, and inherent difficulties in finding suitable anode materials. Though some authors proposed noble metals (*e.g.* Ir) as anode material for small scale demonstration,[2] these are still far from being truly inert in molten oxide electrodes and their cost cannot be afforded for mass production. Similarly, one cannot consider anodic polarization of Mo electrodes in contact with molten oxide electrolytes, in spite of their demonstrated application for electric boosting in glass technology. Therefore, one should consider alternative concepts of consumable electrodes, as currently used in aluminium electrolysis.

Magnetite combines relatively good refractoriness and electronic conductivity[3–7] under operation conditions, at affordable cost for mass production, and may be a candidate for consumable anodes in high temperature pyroelectrolysis.[8,9] Dissolution of magnetite does not add contamination to the system, and may even account for a fraction of iron oxide raw materials. However, the redox stability of magnetite is still limited, mainly if one takes into account that anodic polarization may also promote oxidation of magnetite to hematite, requiring higher operation temperatures to retain magnetite, and raising the issue of limited refractoriness. Thus, the present work attempts to combine the high electrical conductivity of magnetite Fe_3O_4 and improved refractoriness of hercynite ($FeAl_2O_4$) or intermediate spinel type compositions $Fe_{3-x}Al_xO_4$. Note also that alumina is commonly present in iron oxide raw materials, and is also compatible with the expected range of compositions of molten electrolytes in pyroelectrolysis. Phase diagrams predict substantially large compositional domains for $(Fe,Al)_3O_4$ spinels at 1073–1773 K in reducing to inert atmospheres (*i.e.* $p(O_2)$ ranging from 10^{-8} to 0.1 atm).[10,11] Although the phase purity is important, it may not be crucial for application as consumable electrodes, provided that these materials can sustain the conditions of electrolysis in melts and provide sufficient power density. High-temperature

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electrical properties of $Fe_{3-x}Al_xO_4$ spinels were studied for $x = 0.49$ and higher aluminium content,[6] where the conductivity is already significantly lower compared to undoped magnetite Fe_3O_4. Low-temperature conductivity of iron aluminates was also measured as a function of temperature in vacuum.[12] However, no efforts have been made to study the high-temperature electric properties as a function of oxygen partial pressure for small Al content, where the highest values of conductivity (σ) can be expected.

The present work was focused on the analysis of phase relationships, thermal expansion and high-temperature electrical conductivity in the $Fe_{3-x}Al_xO_4$ ($x \leq 1.0$) in oxidizing and inert atmospheres, to determine the most promising material composition, with emphasis on high conductivity and appropriate redox stability at elevated temperatures in mildly oxidizing atmospheres. Complementary static-lattice simulation studies were performed in order to understand the interrelation between the distribution of cations in octahedral and tetrahedral sites of the spinel structure and lattice stability issues. Particular attention is also given to the intermediate temperature range and corresponding spinel-phase metastability, which may become important in terms of the electrode integrity, depending on the operation regime of the electrolysis cell.

2. Experimental

The powders of $Fe_{3-x}Al_xO_4$ ($x = 0.1$, 0.4, 0.7 and 1.0) were prepared by solid state route from stoichiometric amounts of high-purity $FeC_2O_4 \cdot 2H_2O$ and Al_2O_3. Solid state reactions were conducted in air at 1173–1473 K, with multiple intermediate grindings. These powders were compacted in the form of disks or bars at 300–400 MPa and sintered at 1743–1773 K for 10 h in argon atmosphere ($p(O_2) \sim 10^{-5}$ to 10^{-4} atm), with subsequent cooling to room temperature at 3 K/min; hereafter, thus prepared ceramics are referred to as "as-prepared" samples. Other samples were sintered in air, with identical thermal cycle. Experimental density of the ceramics was measured by Archimedes method. For X-ray diffraction (XRD) and thermogravimetry (TG) studies, the ceramics were ground to powders in a mortar.

X-ray diffraction patterns were recorded using a Rigaku D/Max-B diffractometer (Cu Kα, $2\Theta = 10$–$80°$, step 0.02°). High-temperature XRD analysis was made on Philips X'pert MPD equipment in vacuum ($\sim 10^{-7}$ atm). For scanning electron microscopy (SEM, Hitachi S-4100) selected ceramic samples were polished and annealed at several temperatures and oxygen partial pressures. TG studies (Setaram SetSys 16/18 instrument) 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 $Fe_{3-x}Al_xO_4$ ceramics was measured using a vertical alumina dilatometer Linseis L75V/1250 including a gas system with an yttria-stabilized zirconia (YSZ) sensor at the outlet. The measurements were performed on heating (3 K/min) up to 1350 K in argon and air atmospheres. Total 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 simulation was performed using GULP software.[13,14] GULP atomistic simulation is based on the Born model for ionic solids. The charge of atoms in the lattice was considered equal to their formal oxidation state. The interactions between the atoms were formulated in terms of long-range coulombic forces and two types of short-range interactions, namely the Pauli repulsion and van der Waals dispersion. In the present work, a standard Buckingham potential was used for implementation of the short-range forces[13,14]:

$$V_{ij} = A_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - C_{ij} r^{-6} \tag{1}$$

where A_{ij}, ρ_{ij} and C_{ij} are parameters assigned of the pair interactions, and r is the distance between atoms. Polarizability α of the atoms is accounted by core–shell model:

$$\alpha_i = \frac{Y_i^2}{(k_i + f_\Sigma)} \tag{2}$$

where Y_i is the shell charge, k_i is harmonic core–shell spring constant and f_Σ is a sum of the external forces, acting on the shell. For simulation of the magnetite-based spinels, Bush/Woodley potentials sets (Table 1) were selected. To simulate solid solutions, a 2 × 2 × 2 supercell (64 formula units) with 18 Å cut-offs for Buckingham interatomic potentials was used. Four compositions, namely, Fe_3O_4, $Fe_{2.797}Al_{0.203}O_4$, $Fe_{2.5}Al_{0.5}O_4$ and $Fe_{2.297}Al_{0.703}O_4$ were selected for simulation. To resolve possible issues with implicit cation ordering in simulated supercells, a special technique of the random cells generation was elaborated. 8–10 sets of 10 supercells with random distribution of cations in tetragonal and octahedral sublattices were generated for each simulated composition. Each set had a fixed infill of the

Table 1
Phenomenological potentials, used for static lattice simulation.

Atom	Core–shell		Interatomic (Buckingham)				Reference
	Y, e (shell charge)	k, eV/Å^2	Pair	A, eV	ρ, Å	C, eV/Å^2	
O^{2-}	−2.513	20.53	O^{2-}	22.41	0.6937	32.32	[15,16]
Fe_t^{3+}	1.029	10082.5	O^{2-}	1240.232	0.3069	0	[15,16]
Fe_o^{3+}	1.029	10082.5	O^{2-}	1342.754	0.3069	0	[15,16]
Fe^{2+}	2	n/a	O^{2-}	2763.945	0.2641	0	[15,17]
Fel^{3+}	2.957	403.98	O^{2-}	2409.505	0.2649	0	[15,18]