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journal homepage: www.elsevier.com/locate/corsciCoarsening mechanism of LiAlO_2 in acidic and basic molten carbonate saltsSu Jeong Heo^{*}, Junsung Hong¹, Prabhakar Singh^{**}

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ABSTRACT

Long-term corrosion behaviors of molten carbonate fuel cell (MCFC) electrolyte matrix with LiAlO_2 particle coarsening are evaluated in eutectic Li-Na carbonate melts with different $p\text{CO}_2$. In low $p\text{CO}_2$ (basic), the rapid growth of LiAlO_2 particles by Ostwald ripening is observed. TEM analysis verifies the continued process of dissolution and precipitation of LiAlO_2 nanocrystals that promotes LiAlO_2 crystal growth. It is revealed that this growth process is accompanied by α - γ phase transition through a Li_5AlO_4 intermediate phase. In high $p\text{CO}_2$ (acidic) conditions, oriented attachment, primarily between the (003) and (012) planes of α - LiAlO_2 crystals, leads to interparticle coalition and growth.

1. Introduction

Molten carbonate fuel cells (MCFCs) have been regarded as a promising candidate for megawatt scale power systems, because of their high electrical and combined heat and power (CHP) efficiency, low greenhouse gas (GHG) emission from natural gas, and the capability for capturing CO_2 from combustion flue gas [1–3]. Despite significant progress in the past decades, the commercialization of MCFCs still faces challenges such as the long-term corrosion of metallic electrode and bipolar materials [4,5] and dissolution of NiO cathode and LiAlO_2 matrix into the molten carbonate electrolyte, leading to Ni shorting and gas leakage [6–8].

In MCFC, the carbonate ions are oxidized in hydrogen fuel to produce water, carbon dioxide, and electrons at the anode. At the cathode, the carbon dioxide reacts with oxygen from air and is reduced to reform carbonate ions. The presence of steam in the cathode gas atmosphere, as a prospective constituent simulating CO_2 -lean wet atmospheres in commercial MCFC plants, allows for hydroxides to coexist in the molten carbonates [9,10]. Similar to the presence of steam, other gas constituents (H_2 , CO_2 , and O_2), present in anodic and cathodic atmospheres, also interact and influence the stability of electrode, electrolyte matrix, and molten carbonates. For example, the NiO cathode dissolves in the molten carbonate at higher $p\text{CO}_2$ via acidic dissolution reaction leading to the formation of metallic nickel precipitates in the matrix during long term operation with the possibility of causing a short between the two electrodes [11].

On the other hand, α - LiAlO_2 , which is typically used as the electrolyte matrix, remains stable in CO_2 -containing cathodic (i.e., air, 70 % air-30 % CO_2) [12,13] or anodic (80 % H_2 -20 % CO_2 saturated with H_2O) [14] atmospheres. However, the α - LiAlO_2 experiences structural degradation and particle coarsening in low CO_2 atmospheres. Long-term operation can lead to gas cross leakage due to electrolyte migration and depletion [15,16]. In low CO_2 partial pressures, the LiAlO_2 dissociates into Li^+ and AlO_3^{3-} in the molten carbonates by reacting with oxygen ions (O^{2-}) produced by the decomposition of carbonates [17]. Fundamental understanding of the structural stability of the LiAlO_2 at lower CO_2 partial pressures becomes an important part of materials development for designing cell matrix (simulated accelerated dissolution and growth) to achieve durability for over 10-year service life as the dissolved ionic species in the carbonate melt assemble on the surface of remaining LiAlO_2 particles (in contact with the melt) and modify the LiAlO_2 structure [18].

The non-metallic corrosion reactions associated with the dissolution and precipitation are strongly dependent on temperature, LiAlO_2 phase, and the gas atmosphere [19]. We have studied the stability of α - LiAlO_2 under simulated MCFC operating conditions (of various temperatures and atmospheres in the presence of molten carbonate electrolyte) [20]. Our previous observations indicated that the crystalline phase, surface morphology, and surface area of as-prepared α - LiAlO_2 remain unchanged at low temperatures and in high $p\text{CO}_2$ atmospheres, regardless of the oxygen partial pressure, because high $p\text{CO}_2$ suppresses the dissolution of LiAlO_2 in the molten carbonate. In H_2 -containing reducing

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