



Nanostructured gadolinium-doped ceria microsphere synthesis from ion exchange resin: Multi-scale in-situ studies of solid solution formation

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ABSTRACT

In the current nano-sized material revolution, the main limitations to a large-scale deployment of nanomaterials involve health concerns related to nano-dissemination via air. Developing new chemical routes benefiting from nano-size advantages while avoiding their hazards could overcome these limitations. Addressing this need, a chemical route leading to soft nano-particle agglomerates, i.e., macroscopic precursors presenting the ability to be decomposed into nano-sized materials, was developed and applied to $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$. Using cerium/gadolinium-loaded ion exchange resin, the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ solid solution formation as a function of temperature was studied in-situ through X-ray diffraction, X-ray absorption spectroscopy and Raman spectroscopy. Temperatures corresponding to the organic skeleton decomposition and to the mixed oxide crystallization were identified. An optimal heat treatment, leading to nanostructured soft agglomerates, was established. Microsphere processing capabilities were evaluated and particle size distribution measurements were recorded. A very low fracture strength was calculated, and a nanometric particle size distribution (170 nm) was determined.

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1. Introduction

Nanomaterials are often considered a technological breakthrough that can improve materials' performance or give them new properties [1], such as new optical, electronic or magnetic properties [2,3]. Although their synthesis is now well-controlled, their use in fabrication processes remains very complicated due to the risk of spread [4,5]. These risks increase operating cost through the mandatory use of dedicated tools such as glove boxes or clean rooms and in some cases prevent any possibility of utilization [6,7]. Using soft agglomerated nanoparticles can overcome this limitation

or contribute to less restrictive processes. With that in mind, an innovative chemical route based on ion exchange resin was established. The solution proposed here is not to agglomerate previously-synthesized nanoparticles but to synthesize nanostructured and calibrated microspheres which can be decomposed into nano-scale powder by pelletizing or milling, for example. $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ nanostructured microsphere synthesis was selected to illustrate this new route.

Currently, the most studied anode material for Solid Oxide Fuel Cell (SOFC) applications is the Ni-YSZ (nickel and yttria-stabilized zirconia) cermet (ceramic-metal) composite. This composite fulfills a majority of the requirements for an efficient anode, such as high catalytic activity and good electrical conductivity, as well as excellent structural and microstructural integrity under operating conditions. However, its high catalytic activity also induces a major

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drawback due to the presence of Ni. Ni catalyzes the formation of carbon deposits from hydrocarbons under reducing conditions [8]. To solve this problem, gadolinium-doped ceria (GDC) is frequently used as a substitute for YSZ in the Ni–YSZ cermet [9,10]. This mixed-conductor is known to suppress coke formation, and its catalytic behavior in steam reforming of methane has been reported in several studies [11,12]. GDC can also be used on the cathode side (air side) to form a cercer (ceramic–ceramic) composite electrode (e. g., $\text{Pr}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ –GDC composite air electrode) [13]. For such SOFC applications, the synthesis of GDC as porous nanostructured microspheres would be of great interest as precursors for screen printing. Indeed, such soft agglomerates present the ability to be decomposed into nanoparticles during the tri-cylinder milling step required to form a slurry for electrode screen printing [14]. Electrode screen printing will be thus facilitated and gas diffusion to triple phase boundaries improved after electrode sintering.

In a very different context, GDC compounds can be used as non-radioactive surrogates for the $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\delta}$ mixed oxides, called AmBB (Am bearing blankets) and identified as possible targets for Am transmutation. Transmutation of Am into stable or short-lived elements in fast-neutron reactors [15] would be a promising option, currently studied to reduce nuclear waste radiotoxicity. However, AmBB dense pellet fabrication requires special attention due to the high radiotoxicity of Am [16]. Currently, the fabrication of these pellets is based on powder metallurgy processes with ball-milling steps which generate large amounts of fine radioactive particles [17–20]. Dustless processes which eliminate the use of such fine and highly contaminating powders during pellet production are thus mandatory before envisaging an industrial deployment. In this aim, the development of an innovative route using micrometric spherical precursors is studied. Through an adaptation of the weak acid resin (WAR) process [21–25], the general approach consists of elaborating micrometric and brittle spherical mixed-oxide precursors. This geometry was chosen to facilitate the filling of the compaction chamber and subsequent pelletizing. After pelletizing, similar to nanostructured microspheres, obtained pellets are composed of highly reactive nanoparticles allowing for a low sintering temperature. A first step in the demonstration of the feasibility of this process is the use of lanthanide surrogates for uranium and americium, cerium and gadolinium, respectively, as they have chemical properties similar to these actinides [26] and allow many experiments to be performed at lower cost.

Meeting needs of the two above-discussed scientific domains, the development of a spherule route called the calcined resin microsphere pelletizing (CRMP) process has been initiated. In the first part, resin loading with a selected Ce/Gd ratio of 80/20 is described. In the second part, in-situ high temperature characterizations by TGA (thermogravimetric analysis), XRD (high-temperature X-ray diffraction), XAS (X-ray absorption spectroscopy) and Raman spectroscopy of the loaded resin are detailed. These experiments were used to identify the temperature steps (organic skeleton removal steps, crystallization), helping to determine the optimal calcination conditions required to synthesize the target mixed oxide. It also allowed the chemical environment of the cations in the resin and in the oxide to be studied, revealing the evolution of the oxidation degree of lanthanide elements during their mineralization. The oxide microspheres obtained with this process were also characterized by EDS (energy dispersive spectrometry) to measure the obtained Ce/Gd ratio and by SEM (scanning electron microscopy), to observe their microstructure in order to apprehend their future processing behavior. The viability of pelletizing nanostructured microspheres was studied through microsphere pressing and the determination of their fracture strength. Finally, microsphere milling with a tri-cylinder device led to a slurry with nanometric particle size distribution.

2. Experimental

2.1. Precursors

The employed poly-acrylic resin comes from The Dow Chemicals Company (Rohm and Haas, Chauny, France) and consists of an IMAC HP333 gel type acrylic exchanger in the form of micro-spherical beads. Concentrated ammonia solution (25%, Merck, Pro Analysis) and concentrated nitric acid solution (64%, Fisher Chemical, certified ACS Plus) were used in their diluted form (1 M) as washing solutions for resin preparation. Hexahydrate cerium(III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99% purity, Merck) and hexahydrate gadolinium nitrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99% pure, Prolabo) were employed to prepare solutions for resin loading. H_2O stoichiometry of each nitrate was determined by thermogravimetry prior to use.

2.2. Resin metal loading

A batch of microspheres with a 630–800 μm diameter distribution was washed in a column by successive circulation of 1 M aqueous nitric acid solution, deionized water, 1 M aqueous ammonia solution, and finally deionized water, then repeating the complete cycle a second time. This protocol was employed to remove cationic and chemical impurities potentially present in the pores of the microspheres after their industrial synthesis, as well as to convert the resin to its ammonium form. Pre-loading the acrylic resin (protonated form) with labile ammonium ions (NH_4^+) is a necessary step before cationic loading because it fixes the lanthanide ions in substitution for ammonium ions. The resin was then poured into a column with deionized water. In parallel, a 0.5 L aqueous solution of the selected lanthanide elements in stoichiometric proportions was prepared from cerium and gadolinium nitrates in order to get a Ce/Gd ratio equal to 80/20. This stock solution was recirculated through the column filled with the resin batch as long as fixation occurs, i.e., for approximately 16 h. This time was deduced from pH monitoring of the solution showed in Fig. 1, the loading-end corresponding to the stabilization of the pH value. After loading, the resin was washed with deionized water, drained under vacuum and finally dried in an oven at 393 K for 12 h.

2.3. Room-temperature characterizations

The Ce/Gd ratio of the stock solution and dissolved resin was determined by inductively coupled plasma-atomic emission

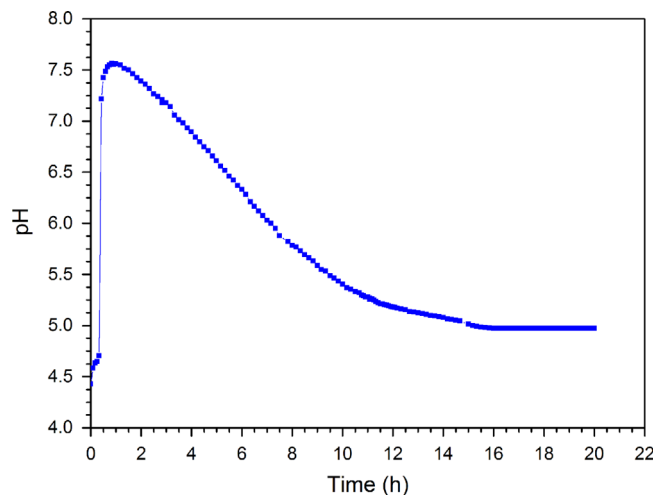


Fig. 1. pH evolution of the (Ce/Gd) solution during resin loading. pH decreases during the experiment from the progressive increase of $[\text{NH}_4^+]$ in solution. The stabilization of pH over 16 h indicates the completion of the cationic exchange.

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