Continuous Hydrothermal Flow Synthesis of Functional Oxide Nanomaterials Used in Energy Conversion Devices

Continuous hydrothermal flow synthesis (CHFS) was used to prepare functional oxide nanoparticles. Materials synthesized include NiO, Y-doped ZrO2, Gd-doped CeO2, LaCrO3 and Ni-substituted CoFe2O4. These types of oxides can be applied in several energy conversion devices, e.g. as active materials in solid oxide fuel cells (SOFCs), oxygen transport membranes (OTMs), and water electrolysis processes. Compared with other chemical synthesis methods, CHFS is advantageous for preparing nanosized materials with a narrow size distribution and a high phase purity. Moreover, CHFS has a high throughput as materials are continuously produced, and the technology can be scaled-up to an industrial-relevant production capacity.

The thesis starts with investigating the most appropriate mixer design for a novel two-stage reactor by computational fluid dynamics modelling. On basis of the modelling results, a two-stage CHFS reactor was constructed, and proof-of-concept syntheses of NiO and Y-doped ZrO2 (YSZ), in both one-stage and two-stage modes, were conducted.

Secondly, Gd-doped CeO2 (GDC) nanoparticles (6 – 40 nm) were synthesized, and the effect of the pH on their size, morphology and composition was studied. An up-scaled synthesis of Gd0.2Ce0.8O2-δ nanoparticles was made, and the as-synthesized particles were processed into inks that displayed a good printability in inkjet printing of electrolytes on both green NiO-GDC and pre-sintered NiO-YSZ substrates. Particularly on the pre-sintered NiO-YSZ substrate, dense continuous layers (< 2 μm in thickness) composed of GDC and YSZ that fully covered the substrate were obtained after firing at 1300 °C.

In addition, (La0.6Sr0.4)0.99CoO3 – Gd0.2Ce0.8O2-δ (LSC-GDC) core-shell type particles were prepared and their high-temperature microstructural evolution was studied in two different sintering processes, i.e. spark plasma sintering and conventional sintering. By conventional hydrothermal batch-type synthesis, a core-shell structure was realized by precipitating ~6 nm large GDC particles on the surface of LSC particles under a mild hydrothermal condition of 100 °C resulting in an integral GDC shell around the LSC core. It was found that by spark plasma sintering, a fine microstructure containing nanograins could be obtained and the graded core-shell architecture could be partially maintained.

For the first time, phase-pure LaCrO3 was obtained by CHFS without any post treatments. A continuous production of cube-shaped LaCrO3 particles (639 nm) was achieved. Processing parameters (temperature and alkali concentration) were found to affect the phase purity of the obtained particles significantly. The synthesized LaCrO3 particles were used to prepare 10Sc1YSZ – LaCrO3 dual-phase oxygen transport membranes. A density of ~90 % was achieved after firing at 1400 °C, which is below normal sintering temperatures for LaCrO3-based ceramics. Oxygen permeation fluxes up to 5 × 10-8 mol cm-2 s-1 were obtained with a 1 mm thick membrane tested in air/N2 at 900 °C.

Finally, CoFe2O4 and Ni-substituted CoFe2O4 nanoparticles were prepared by CHFS and their catalytic properties were evaluated. The CoFe2O4 was found to be active for catalytic CO oxidation. A 50 % conversion of CO at 223 °C and a complete conversion at 310 °C was reached. By CHFS, Ni-substituted CoFe2O4 nanoparticles with controlled Ni contents were synthesized, and their activity as catalysts for the oxygen evolution reaction (the half reaction of water electrolysis) was evaluated. Whereas no simple correlation between the activity and the Ni content was detected, a remarkable improvement of the activity was observed for the sample with 30 at% (in atomic percent) Ni-substituted CoFe2O4 (Co0.7Ni0.3Fe2O4) compared to all other investigated compositions.

Overall, the thesis demonstrates the versatility of the CHFS route for preparing functional oxides in nano particulate form, and documents the properties of the synthesized materials in a number of specific applications (fuel cells, membranes and catalysis).

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