NANOCOFC APPROACH TO DEVELOP ADVANCED 300-600^{o}C FUEL CELLS

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Introduction

The challenges facing the SOFCs are critical where the materials cause the key issue [1, 2]. An electrolyte conductivity of 0.1 S/cm is a basic requirement for high performance SOFCs. This high temperature prevents commercialization due to high costs and technical complexity. Designing and development of functional materials at lower temperatures is therefore a must and a big challenge. Many efforts are done to lower the temperature by using thin-film technologies on yttrium stabilized zirconia (YSZ). But a thin film electrolyte can not guarantee long life since FC operation involves mass transport processes which can affect the electrolyte property in one or another aspect, thus causing serious degradation. Moreover, the thin film YSZ SOFCs cannot be operated bellow 700 ºC.

Manipulation of interphases of nanotech based composites, so-called nanocomposites can tremendously reduce working temperature of conventional SOFC from 1000^{o}C to 300-600^{o}C. The 300-600ºC FC technology is the gap among existing fuel cell technologies which has not been developed due to lack of functional materials as a fact in such a long history of the fuel cell R&D. The European Union project NANOCOFC ("Enhancement of Research Capabilities on Multi-functional Nanocomposites for Advanced Fuel Cell Technology through EU-Turkish-China Cooperation , EC FP6 NMP SSA Contract No 32832) is one of the main platforms in Europe for low temperature (LT) SOFC R&D. Superionic conduction reaching 0.2 S/cm at around 300 ^{o}C and 1200 mW/cm^{2} obtained at 500 ^{o}C have been reported [3, 4].

Experimental

The nanocomposites are based on two-phase materials. One is the ion-doped ceria, e.g. samarium or gadolinium doped ceria (SDC or GDC) and another is a salt, e.g. carbonates, or metal oxides. The two-phase nanocomposites were prepared through wet chemical processes and detailed experiments were reported before [3, 4].
The nano-characterizations on structure and microstructure were carried through XRD (Philips X'pert pro super Diffractormeter), scanning electron microscope (SEM A Zesiss Ultra 55) and transmission electron microscopy (TEM, JEOL JEM-2100F). The electrical properties were studied through electrochemical impedance spectra (EIS) (Princeton VersaSTAT, Galvanostat/Potentiostat). The LTSOFCs were constructed by using the ceria-based two-phase nanocomposites as the electrolytes and mixed nickel and copper oxides as the anode, and lithiated nickel oxide as the cathode. The measurements were performed between 300-600ºC.

Result and discussion

Figure 1 shows a typical ceria-based two-phase nanocomposites of the SDC-Na_2CO_3, where the core-shell structure can be clearly identified. The superionic conduction was discovered at around 300ºC and the conductivity reached 0.1 S/cm [3]. In the two- phase nanocomposite materials the two-phase co-existence creates the interfaces and particle surfaces between the constituent phases, where the superionic conduction takes place.

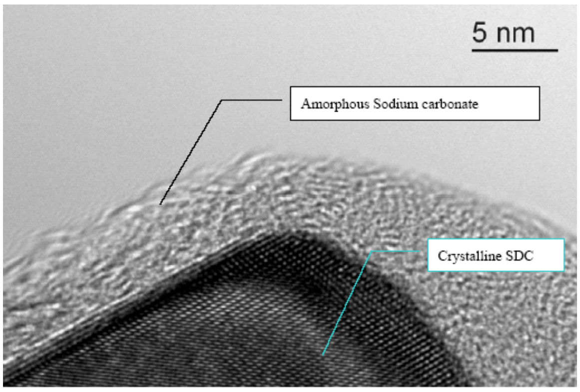

Figure 1: Core-shelled SDC-Na_2CO_3 nanocomposite analyzed by TEM (after ref. 3)

The core-shell is not the only way to create functional structure/interfaces for sueprionic conduction. Many other types of the nanocomposites are developed as long as they can able to create interfaces between the two phases as "ion highways". For example, in the homogenous SDC-$LiNaCO_3$, the interfaces can be constructed as continuous framework between the two-constituent SDC and $LiNaCO_3$ phases. The nanocomposites based on nanowires are another type of the functional material, where nanowires provide ion long-distance conduction highways. We have successfully synthesized the diameter of the SDC nanowires ranging from 100 to 200 nm and about 10 μm long. The TEM image, in displays the SDC nanowires exhibit uniform size and the diameter of individual SDC nanowire is about 100 nm, which agree well with SEM results. The texture of a single nanowire is observed to be poly-crystalline with recognizable boundaries or voids [5]. The SDC nanowires in the composite can be optimized and better aligned to achieve superionic conductivity. It is certainly a very potential electrolyte material, since one dimensional nanowire structure is supposed to have longer continuous conductive path at interfaces in nanocomposite electrolyte.

It is common that nano-particle size in single-phase materials can, on one hand, create large particle surfaces, but on the other hand the particles are not stable due to high surface energy and the active and chemically unbounded situation. In two-phase materials large use of the appropriate 2nd phase material/particles can create interfaces and surfaces with effective functions in two-phase nano-particles while, in the same time it can stabilize and modify the surface properties. Our recent core-shell ceria-carbonate nanocomposites have shown a good thermal stability compared to single-phase ceria [6].

The two-phase nanocomposites can overcome the single-phase ceria side-effects and makes it possible to apply nanomaterials to a new field of SOFC R&D, since the surface energy and diffusion rate of the nanostructured materials are greatly modified by accession of the second phase materials, resulting in suppression of both grain growth under high temperature and electronic conduction.

Using functional nancomposites as the electrolytes the advanced LTSOFC technology has been demonstrated [3, 4]. Further impedance analysis was performed on the fuel cells. Figure 2 shows typical electrochemical impedance spectra (EIS) for the SDC-Na_2CO_3 nanocomposites at 470 ^oC. The results presented in table 1 are obtained by modeling of the EIS with a standard equivalent circuit configuration using the Zview software. The inductance L may be caused by the stainless tube of the measurement device. The ohm resistance, R_1, indicates the electrolyte resistance. The electrochemical resistance, R_2, is probably associated with the electrode process combined cathode and anode reaction. CPE_1 is the constant phase element, mainly caused by the interfaces between anode together with cathode and anode. As we can see from table 1, the electrolyte resistance, 0.366 Ωcm^2 is significantly smaller than that, 0.555 Ωcm^2 of the electrode polarization resistance. It can be addressed that the electrode polarization process is predominant in rate determination. This indicates the fuel cell performance is mainly limited by the electrolyte and electrode interfaces. Thus further development of compatible electrodes with high catalyst functions that can significantly reduce the electrode polarization losses are strongly required to develop high performance low temperatures fuel cells.

Table 1: the ohm resistances (R_1), polarization resistances (R_2) and total resistances (R_t) of fuel cell

R_1 (Ωcm^2)	**R_2 (Ωcm^2)**	**R_t (Ωcm^2)**
0.366	0.555	1.021

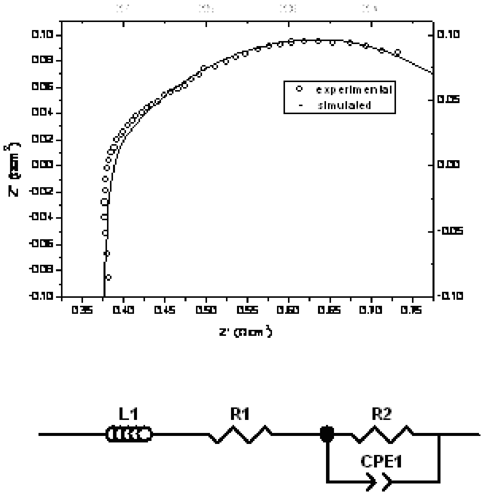

Fig.2: EIS was obtained from the fuel cell at 470ºC and equivalent circuit used in simulation.

Conclusion

The two-phase nanocomposites for advanced fuel cell technology (NANOCOFC) have been demonstrated as a powerful new approach to develop 300-600ºC fuel cell technology. Several types of nanocomposites in core-shells, homogenous frameworks or nanowires are recognized with interfacial superionic conduction and other functionalities to overcome the single nano-phase ceria problems with great potential to develop advanced 300-600ºC fuel cell technology. The EIS characterization indicates that the fuel cell performance is mainly limited by the electrolyte and electrode interfaces. Development of the compatible electrodes with high catalyst functions is highly required.

References

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