Optimisation of perovskite anodes for real fuels in SOFCs

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Conventional SOFCs utilise nickel zirconia cermet electrodes that have excellent catalytic and electrochemical performance and exhibit good conductivity. Unfortunately, nickel is also an excellent catalyst for hydrocarbon cracking, thus these cermets can only be utilised in hydrocarbon fuels if excess steam is present to ensure complete fuel reforming, diluting fuel and adding to system cost. Equally problematic, is the poor redox tolerance of nickel cermets, that precludes many medium- and small-scale applications. Thus there is considerable interest in finding an alternative anode system.

The most commonly used anode materials for zirconia-based SOFCs are Ni/ZrO_2 cermets, which display excellent catalytic properties for fuel oxidation and good current collection but do exhibit disadvantages, such as low tolerance to sulphur[1] and carbon deposition[2] when using hydrocarbon fuels and poor redox cycling causing volume instability. The nickel metal in the cermet tends to agglomerate after prolonged operation, leading to a reduced three-phase-boundary and increasing resistance. There are preliminary reports that the problem of carbon deposition when using hydrocarbons in a SOFC may be avoided by using a Cu-ceria anode[3] or when an $(Y_2O_3)_{0.15}(CeO_2)_{0.85}$ interface was applied between YSZ and Ni-YSZ cermet anode although only at lower temperatures[4]. The potential agglomeration of metal components in the cermet anode and certainly the redox stability could still be problematic, however.

Perhaps this problem may be solved by application of a single-phase material as an SOFC anode. Different structure types, such as perovskite, fluorite, pyrochlore and tungsten bronze have been investigated as potential anode materials. Interesting results have been obtained with lanthanum strontium titanates and especially cerium doped lanthanum strontium titanate[5]; however, it is now thought that the cerium doped anodes are in fact two phase consisting of a ceria/perovskite assemblage.

$LaCrO_3$-based materials have been investigated as interconnect materials for SOFCs; however, they are also potential anode materials for SOFCs due to their relatively good stability in both reducing and oxidising atmospheres at high temperatures. The reported polarization resistance using these materials is too high for efficient SOFC operation, although significant improvements have been achieved using low level doping of the B-site. Quite a lot of attention has been focused on 3% replacement of Cr by V and although methane cracking seems to be avoided[6], the polarisation resistance is still of the order 10 Ωcm^2 The introduction of other transition elements into the B-site of $La_{1-x}Sr_xCr_{1-y}M_yO_3$ (M = Mn, Fe, Co, Ni) has been shown to improve the catalytic properties for methane reforming[7]. Of the various dopants, nickel seems to be the most successful and the lowest polarisation resistances have been reported for 10% Ni-substituted lanthanum chromite; however, other workers have found nickel exolution from 10% Ni-doped lanthanum chromates in fuel conditions.

In this report, double perovskites based upon Cr, Ga and Nb and one or more other transition elements (M) such as V, Mn, Fe, Co, Ni, Cu at the B-sites forming compositions $(La,Sr)_2M_{1-x}M'_{1+x}O_{6-\delta}$ have been investigated. Previous workers have focused upon low doping levels of up to 20% dopant on the B-site. Here we report on double perovskites where two metal species occupy the B-site in excess of the percolation limit (e.g. >33%). Such dramatic replacement of an active B-site ion by another element would normally significantly degrade its functionality; however, if the two elements act in a complementary fashion, then a dramatically improved new material may be achieved. Samples containing ~50% Co, Ni or Cu were clearly unstable under fuel conditions, with very significant exsolution of metal. This is not surprising, as these oxides are unstable, with respect to reduction to the metal under fuel conditions, fig 1. The stability limit for FeO is very close to fuel conditions; however, MnO is clearly stable under fuel conditions. Mn, like Cr or Fe supports p-type conduction in oxidising conditions, but has previously been shown to promote electroreduction under SOFC conditions[8]. Furthermore, Mn is known to accept lower co-ordination numbers in perovskites and so may enhance oxide-ion migration by facilitating vacancy migration.

This approach has been found to be successful with area specific resistances as low as 0.3Ωcm^2 being achieved at 900^oC for a $(La,Sr)MnCrO_3$ perovskite, comparable to nickel cermets, but with good redox stability and hydrocarbon cracking resistance, even in fairly dry conditions.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
MO_5			V^V		✓	✓	✓	✓	Cu^{II}	
MO_4*tet*			V^V		?	✓	?	?		
MO_4*Sq*								?	Cu^{II}	
Fuel	✓	✓	✓	✓	✓	?				

Figure 1 Scheme of fuel stability and reduced oxygen co-ordination available for transition metal perovskite oxides

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