Short term stability of (M, Mn or Fe)$_3O_4$ spinel Layer for SOFC Stacks

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Introduction

Solid oxide fuel cells (SOFCs) are very energy efficient energy generation technology. However, SOFCs need to operate at high temperatures and are therefore susceptible to cathode poisoning due to upstream chromium evaporation. To mitigate this issue, as an electrically conductive (Mn, Co)$_3O_4$-CeO spinel coating was developed at PNNL. The Mn-Co-O spinel contains Co, which is a relatively expensive material. Hence, if a cheaper element can be substituted, it could substantially reduce manufacturing costs. Last year, we presented the synthesis and coating optimized conditions. This paper summarizes recent efforts to replace Co with Ni or Cu and Mn with Fe.

Objective

Prevent Chromia species evaporation and maintain stable electrical conductive layer. Search for cost reducing alternative spinel material.

Issue and idea

The price of the Cobalt is $28.5 (USD)/Kg. In the case of manganese, the price is $2.12 (USD)/Kg. The copper price is $6.19 (USD)/Kg, and the nickel price is $13.44 (USD)/Kg. In the case of iron, the available data is only for the iron ore fines. The price of iron ore fines is $0.1 (USD)/Kg. The cost of each element is 9%, 16%, and 0.1% of cobalt price if we use copper, nickel, and iron respectively. (7/9/2020-Trading Economics)

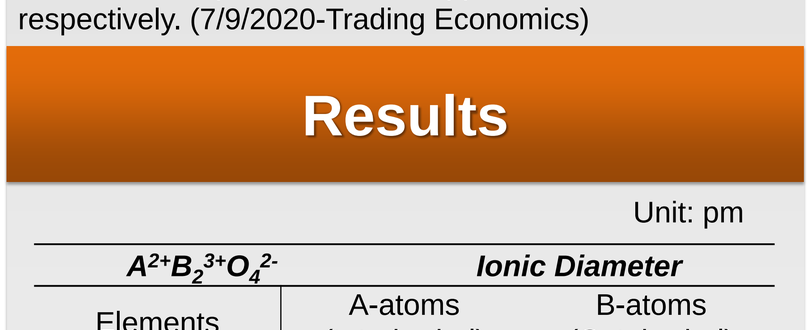
Results

Unit: pm

$A^{2+}B_2^{3+}O_4^{2-}$	*Ionic Diameter*	
Elements	A-atoms (tetrahedral)	B-atoms (Octahedral)
Co	72	68.5
Mn	80	72
Cu	71	68
Ni	69	70
Fe	77	69

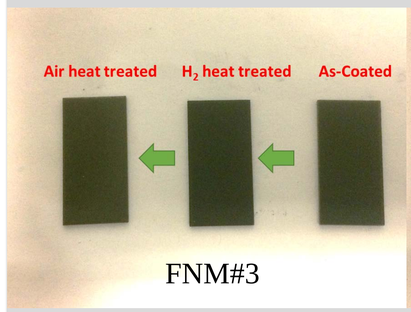
Candidate of spinel system

Spinel system	*Possible composition*	
$(Cu, Mn)_3O_4$	FCM#1	FCM#2
$(Ni, Mn)_3O_4$	FNM#3	FNM#4
$(Cu, Fe)_3O_4$	FCF#5	FCF#6

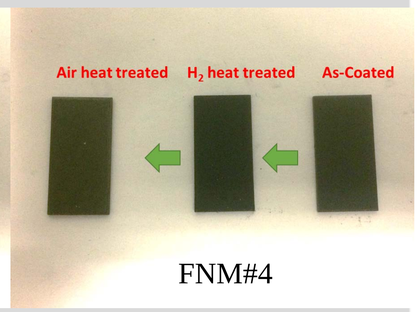


FCM#1

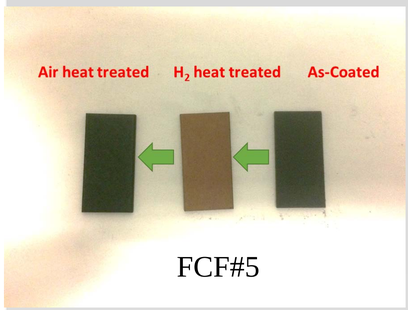
FCM#2



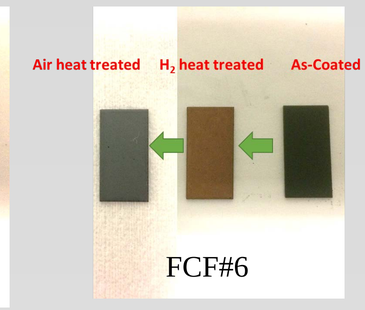
FNM#3



FNM#4



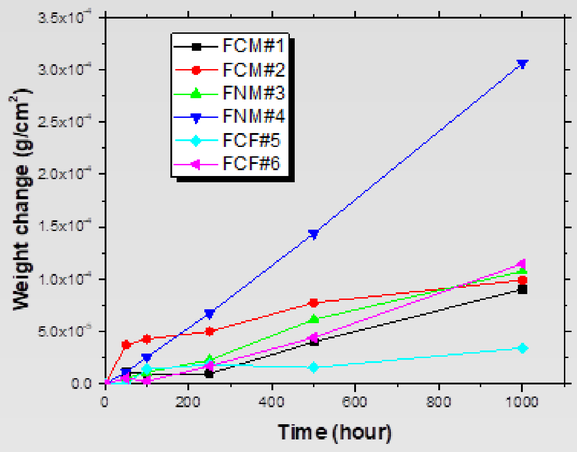
FCF#5



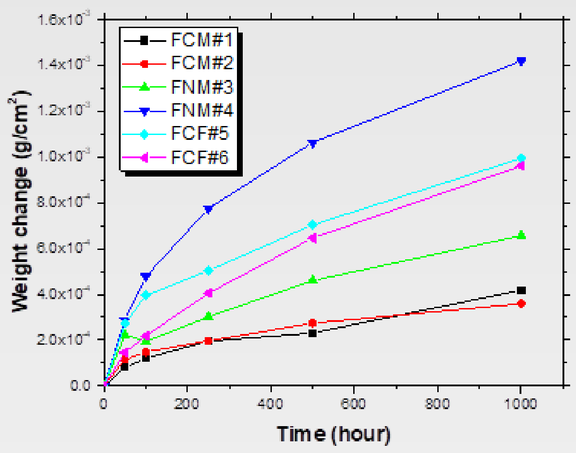
FCF#6

Iso thermal test

800℃

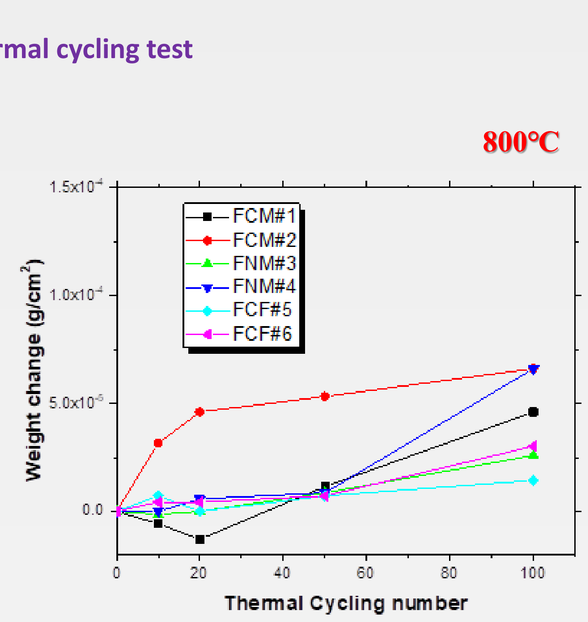


900℃

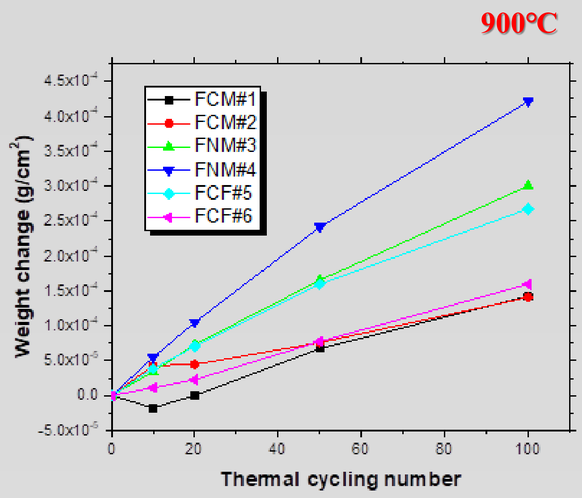


thermal cycling test

800℃



900℃



Summary

The iso-thermal test at 800℃ shows the FCF#5 has more oxidation resistance than others. The FNM#4, which has more Mn element than FNM#3, shows a more oxidation rate. If the temperature goes up to 900℃, the same series spinel making a group. However, the FNM series shows a significant difference, as shown at the 800℃ result. The FCM series shows excellent higher temperature oxidation resistance. In the case of thermal cycling, the result indicates a very similar effect to the iso-thermal test. However, the oxidation result shows FNM#3 is not lower than the FCF series. All materials show a lower oxidation rate than without protective coating.

ABOUT

Pacific Northwest National Laboratory

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Acknowledgements

The U.S. Department of Energy's National Energy Technology Laboratory (NETL) funded the work summarized in this paper as part of the Solid Oxide Fuel Cell Core Technology Program. Battelle Memorial Institute operates PNNL for the U.S. Department of Energy under Contract DE-AC06-76RLO1830.

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