# Auxiliary Electrodes for Chromium Vapor Sensors

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Measurement of chromia-containing vapors in solid oxide fuel cell systems is useful for monitoring and addressing cell degradation caused by oxidation of the chomia scale formed on alloys for interconnects and balance-of-plant components. One approach to measuring chromium is to use a solid electrolyte with an auxiliary electrode that relates the partial pressure of the chromium-containing species to the mobile species in the electrolyte. One example is $YCrO_3$ which can equilibrate with the chromium-containing vapor and yttrium in yttria stabilized zirconia to establish an oxygen activity. Another is $Na_2CrO_4$ which can equilibrate with the chromium-containing vapor to establish a sodium activity.

## Chromium Poisoning

One of the major advantages of SOFCs is that, due to their high operating temperatures, they are tolerant of the type and purity of the fuel used [1-7]. However, the higher operating temperatures that increase reaction rates in the fuel, and thus enhance fuel flexibility, also increase the rates of undesired reactions and cause degradation of the fuel cell components. One of the major degradation mechanisms in SOFCs is cathode poisoning by chromium from vaporization of the metallic interconnect material [7,8].

Chromium poisoning of SOFC cathodes occurs by gas-phase transport of chromium from the interconnect material to the cathode. The chromium transport occurs primarily through the formation of $Cr^{6+}$-containing species, such as $CrO_3$ or $CrO_2(OH)_2$, from oxidation of $Cr_2O_3$ formed on the interconnect [9-17]. Chromium poisoning has been observed in chromium-based [18,19], nickel-based [20-23] and iron-based [24-38] interconnect alloys, so one of the objectives in the design of new alloys for SOFC interconnects is to reduce scale volatilization. One alloying addition used to reduce volatilization is manganese, which is incorporated in the oxide scale and leads to the formation of a $(Mn,Cr)_3O_4$ spinel layer on the scale surface. The reduced chromia activity in the outer spinel phase reduces chromium volatilization and thus reduces, but does not completely eliminate, chromium poisoning. To further reduce the chromium volatilization to the levels required for long-term applications, ceramic coatings are applied to the metallic interconnect materials [39,40]. In general, a degradation mechanism based on volatilization is expected to be enhanced with increasing temperatures. Although such an increase in the amount of degradation with increasing temperature has been observed [31], this is not always the case. For example, Kaun *et al.* [30] and Kim *et al.* [41] reported that the amount of degradation increased as the temperature was decreased from 800ºC to 700ºC and 850ºC to 750ºC, respectively. In

addition, chromium poisoning has been observed at temperatures as low as 600ºC [28]. One of the reasons for this unexpected temperature dependence is that the temperature dependence of the equilibrium partial pressure of the predominant chromium-containing species, $CrO_2(OH)_2$, is relatively low [11,16,17], so factors other than the vapor pressure of the chromium containing species determine the deposition rate. Although either $CrO_3$ or $CrO_2(OH)_2$ can be reduced to form $Cr_2O_3$ and lead to chromium poisoning, the presence of water vapor increases the partial pressure of $CrO_2(OH)_2$. The partial pressure of $CrO_2(OH)_2$ in air is higher than that of $CrO_3$ for typical SOFC operating temperatures (*i.e.* 800°C).

Although the amount of chromium volatilization can be reduced using coatings, failure of the coatings during operation could lead to chromium poisoning. Thus, measurement of the chromium content in the gas during operation would be valuable to detect such failure earlier so that appropriate changes in the operating parameters or maintenance procedures can be implemented.

In addition, to reduce or eliminate the detrimental impact of chromium poisoning, systems for capturing chromium-containing gases within the SOFC balance of plant are being developed [42]. Measurement of the chromium partial pressure within or near such a system would provide valuable information for monitoring the health and effectiveness of the system.

## Chemical Sensors

Since the pioneering work of Kiukkola and Wagner [43] demonstrating that solid electrolytes could be used in galvanic cells to measure the thermodynamic properties of oxides, solid electrolytes have been used in chemical sensors. The ionic conduction in solid electrolytes is thermally activated and thus its rate increases with increasing temperature, so solid electrolytes are well-suited for high temperature applications such as in SOFCs. In addition, solid-state devices, such as those based on solid electrolytes, can be miniaturized [44,45], which provides opportunities for local measurement of gas compositions.

Sensors for which the output is an open-circuit voltage are referred to as potentiometric sensors and can be used for a wide variety of species [46-51]. The measured voltage can be established by a thermodynamic equilibrium or by a non-equilibrium steady state between electrochemical reactions at the electrode. Sensors based on measurement of thermodynamic equilibrium are preferred for long-term applications because their responses are less dependent on factors that affect electrode kinetics, such as surface area changes from microstructural coarsening.

The voltage generated across a solid electrolyte is determined by the difference in the concentration of the species that is mobile in the solid electrolyte. However, an additional phase, referred to as an auxiliary electrode, can be added to provide a link between the target species and the species to which the electrolyte responds by equilibrating with both phases. In some cases, the electrolyte material can provide this function, so a separate auxiliary phase need not be added. One example is the use of sodium β-alumina as an oxygen sensor [52-54] where the $Na_2O$ in the electrolyte equilibrates between oxygen gas and sodium ions. One advantage of this approach is that

β-alumina remains a pure ionic conductor to very low oxygen partial pressures. A similar approach has been used with the fluoride ion conducting electrolytes $MgF_2$ [55] and $LaF_3$ [56] in sensors for measuring the concentrations of magnesium and lanthanum, respectively, in molten aluminum.

Solid electrolyte sensors have excellent stability in aggressive environments. For example, solid electrolyte based sensors have been used in the characterization of molten metals [57-59]. The most widely used electrochemical sensor for molten metals is the oxygen sensor for molten steel [60-62]. In addition to oxygen sensors, solid electrolyte based sensors for measuring the amount of sulfur [63-65] and nitrogen [65,66] in dissolved in steel have been developed.

Oxygen Ion Conducting Electrolyte

Sensitivity to chromium vapor can be provided using an oxygen ion conducting electrolyte with an auxiliary electrode, which is a principle demonstrated in numerous systems including for measuring chromium in molten steel. Specifically, $Cr_2O_3$ has been used as the auxiliary electrode in a chromium sensor for molten steel [67], where the oxygen activity at the sensing electrode is established by Equation 1,

$$2\underline{Cr}\ (in\ iron) + 3O^{2-} = Cr_2O_3\ (s) + 6e^- \qquad [1]$$
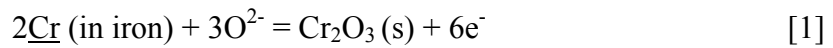
where $\underline{Cr}$ (in iron) represents chromium dissolved in the molten steel. An analogous reaction could be used to measure the partial pressure of $CrO_3$ according to Equation 2.

$$Cr_2O_3\ (s) + 3O^{2-} = 2CrO_3\ (g) + 6e^- \qquad [2]$$
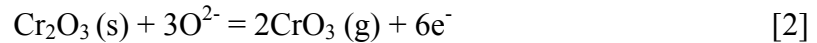
A similar approach can be used to measure the concentration of a chromium-containing vapor. However, if $Cr_2O_3$ were used as auxiliary electrode it could oxidize and contribute to the chromium volatilization. Thus, an auxiliary electrode with a lower $Cr_2O_3$ activity must be used. For example, $LaCrO_3$, which has previously been used as the interconnect in SOFC systems [68] could be used as the auxiliary electrode. However, establishing a fixed $Cr_2O_3$ activity would require including $La_2O_3$ in the equilibrium. Zirconia can be doped with lanthana to provide a fixed $La_2O_3$ activity. However, zirconia is more commonly doped with yttria, i.e. yttria stabilized zirconia (YSZ), so the oxygen potential could be related to the $CrO_3$ partial pressure using $YCrO_3$ as the auxiliary electrode. The $Y_2O_3$-$Cr_2O_3$ phase diagram [69] indicates that $YCrO_3$ is the only mixed oxide in the system. In addition, the $ZrO_2$-$Y_2O_3$-$Cr_2O_3$ ternary phase diagram [77] shows that $YCrO_3$ is stable with the yttria-doped zirconia cubic phase. Thus, the electrode potential can be established according to Equation 3.

$$2YCrO_3\ (s) + 3O^{2-} = 2CrO_3\ (g) + Y_2O_3\ (in\ YSZ) + 6e^- \qquad [3]$$
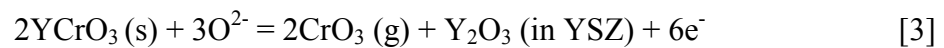
With the formation of $CrO_2(OH)_2$, which has a high partial pressure in humid environments as shown in Figure 1, the electrode potential can be established by Equation 4.

$$2YCrO_3\ (s) + 2H_2O\ (g) + O^{2-} = 2CrO_2\ (OH)_2(g) + Y_2O_3\ (in\ YSZ) + 2e^- \qquad [4]$$
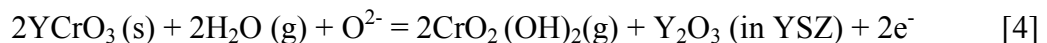
Note that the electrode potential, depends on the water vapor partial pressure, so the water vapor content in the gas will need to be monitored to properly interpret the sensor signal

The reference electrode could be a metal / metal-oxide mixture. Using chromium, which would establish the potential according to Equation 5,

$$2Cr\ (s) + 3O^{2-} = Cr_2O_3\ (s) + 6e^- \qquad [5]$$
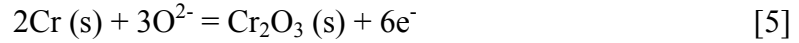
would be the most straight-forward approach. For sensing $CrO_3$, the overall cell reaction would be described by,

$$2YCrO_3\ (s) + Cr_2O_3\ (s) = 2CrO_3\ (g) + 2Cr\ (s) + Y_2O_3\ (in\ YSZ) \qquad [6]$$
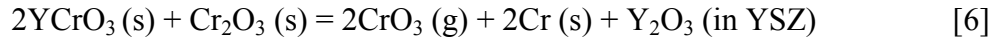
which is from the combination of Equations 3 and 5. Other metal / metal-oxide mixtures could also be used and may be desired to achieve a different voltage output.

A sensor was fabricated using a YSZ electrolyte, a Pt paste reference electrode and a $YCrO_3$ auxiliary electrode as shown in Figure 1. The sensor was tested with and without a $Cr_2O_3$ pellet being place adjacent to the sensor. After the sensor output reached a constant value, the resistance of the cell was measured. The current generated from this measurement disturbed the cell, which provided a mechanism to determine if the output would return to the original value. The times in the example outputs of the sensors shown in Figure 2 are referenced to this electrical resistance measurement. The magnitudes of the sensor output are low and increase with decreasing temperature. The difference between the responses with and without chromium present is small.
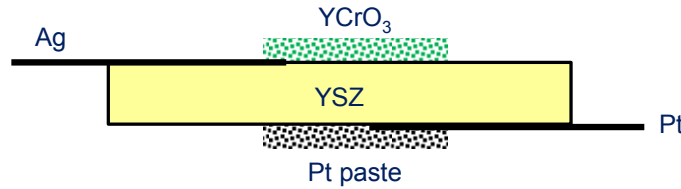


Figure 1. Schematic of chromium sensor.

Sodium Ion Conducting Electrolyte

Sensors can be developed with electrolytes that conduct ions other than oxygen. There are several sodium ion conducting electrolytes, the most appropriate of which for a high temperature sensor due to its high conductivity and good stability is beta alumina [71]. A sodium-containing auxiliary electrode, such as $Na_2CrO_4$, would provide response to $CrO_3$ according Equation 7,

$$2Na_2CrO_4\ (s) = 4Na^+ + 2CrO_3\ (g) + O_2\ (g) + 8e^- \qquad [7]$$
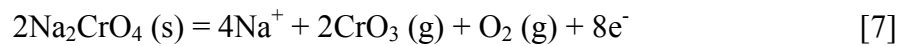
or to $CrO_2(OH)_2$ according to Equation 8.

$$2Na_2CrO_4\ (s) + 2H_2O\ (g) = 4Na^+ + 2CrO_2(OH)_2\ (g) + O_2\ (g) + 4e^- \qquad [8]$$
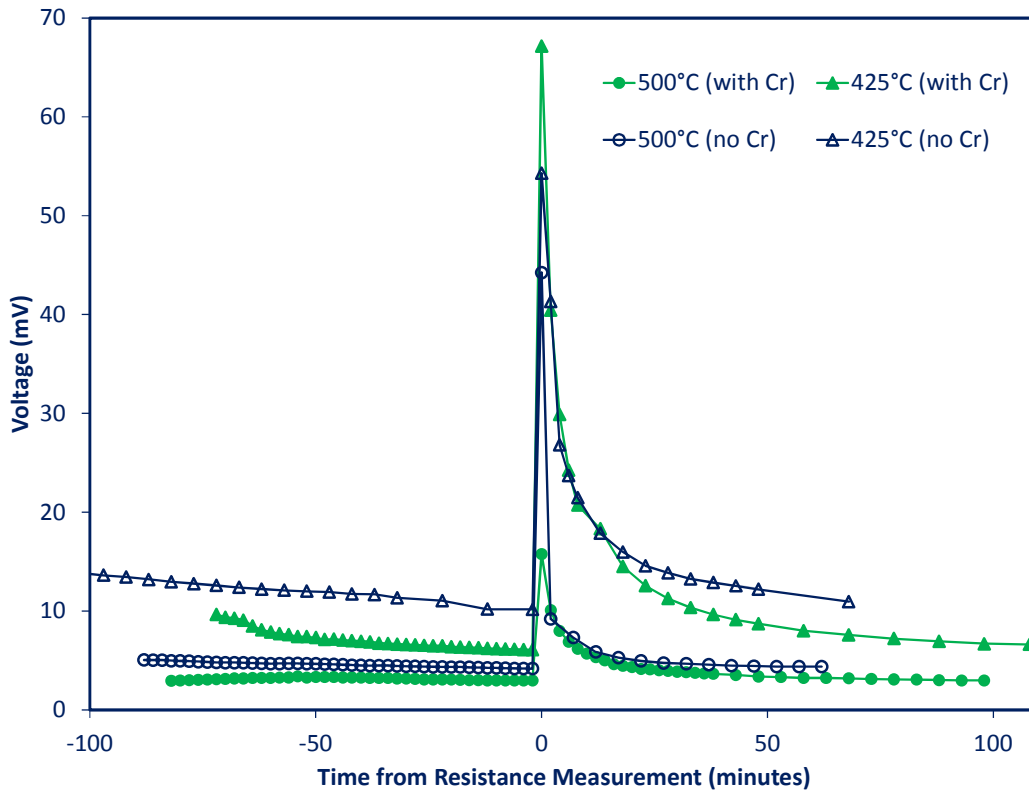
Figure 2. Output of sensor Pt, Pt paste │ YSZ │ YCrO₃, Ag. The times are referenced to the time at which the cell resistance was measured to disturb the cell.

The reference potential could be established using the same auxiliary electrode with a chromium / $Cr_2O_3$ mixture according to Equation 9,

$$3Na_2CrO_4 \text{ (s)} + 5Cr \text{ (s)} = 6Na^+ + 4Cr_2O_3 \text{ (s)} + 6e^- \qquad [9]$$

in which case the overall cell reaction is given by Equation 10

$$8Cr_2O_3 \text{ (s)} + 6H_2O \text{ (g)} = 10Cr \text{ (s)} + 6CrO_2(OH)_2 \text{ (g)} + 3O_2 \text{ (g)} \qquad [10]$$

Alternatively, mixtures of sodium-cobalt oxides have been shown to provide a stable reference potential in gas sensors using sodium-ion conducting electrolytes [72,73].

## Conclusions

Solid electrolyte based sensors offer a potential method for measurement of chromium containing gases. Because chromium-containing solid electrolytes are not available, auxiliary electrodes are needed to relate the chromium concentration to the activity of the mobile species. Potential electrode materials for use with oxygen ion conducting and sodium ion conducting solid electrolytes are available. The output of a sensor based on a YSZ electrolyte and YCrO₃ auxiliary electrode was small with little response to the presence of chromium.

## Acknowledgments

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