



## Sulfur-Tolerant Cathode Materials in Electrochemical Membrane System for H<sub>2</sub>S Removal from Hot Fuel Gas

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The chemical and electrochemical stabilities of some sulfur-tolerant materials have been studied for use as cathodes in an electrochemical membrane system that removes H<sub>2</sub>S from hot fuel gas streams. The typical fuel stream inlet composition at 650-750°C and 1 atm was 34% CO, 22% CO<sub>2</sub>, 35% H<sub>2</sub>, 8% H<sub>2</sub>O, and 0.2-2% (molar) H<sub>2</sub>S. Among the compounds studied, Gd<sub>2</sub>TiMoO<sub>7</sub> and La<sub>0.7</sub>Sr<sub>0.3</sub>VO<sub>3</sub> exhibited the best stability when exposed to fuel streams containing high concentrations of H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O. The electrical conductivities of Gd<sub>2</sub>TiMoO<sub>7</sub> and La<sub>0.7</sub>Sr<sub>0.3</sub>VO<sub>3</sub> were 6 and 30 S cm<sup>-1</sup>, respectively, as measured at 650°C in 4% H<sub>2</sub> balanced with argon. They also showed adequate microstructural stability at temperatures up to 750°C. However, Gd<sub>2</sub>TiMoO<sub>7</sub> had better stability with molten electrolyte (Li<sub>0.62</sub>K<sub>0.38</sub>CO<sub>3</sub>) present, whereas La<sub>0.7</sub>Sr<sub>0.3</sub>VO<sub>3</sub> had better stability in the sour gas stream without molten electrolyte present. Accordingly, a layered electrode that could help preserve a stable environment for each of these compounds is a promising candidate electrode for the application.  
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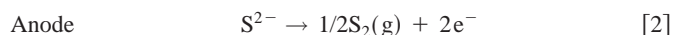
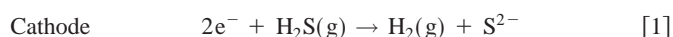
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### Significance of H<sub>2</sub>S Removal

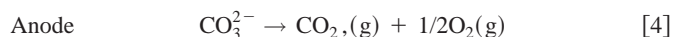
Fossil fuels supply a majority of the world's electricity and combustible fuel. Before these fuels are used for power generation, contaminants must be removed from the fuel. Sulfur is the most predominant and problematic contaminant. In fuel reforming or gasification at high temperature, hydrogen sulfide is formed. H<sub>2</sub>S is not only toxic to humans at levels of 20 ppm, but it is also capable of corroding metals and thus irreversibly damaging equipment such as turbines and electrodes. It can also poison catalysts such as those used in Fischer-Tropsch and hydrotreating processes.

Current methods of removing H<sub>2</sub>S usually involve low-temperature absorption or high-temperature adsorption followed by postregeneration of the sorbent. To compete with these methods, research toward optimizing a high-temperature, continuous, electrochemical membrane system (EMS) has been underway for some time. First patented in 1980,<sup>1</sup> full-cell runs utilizing graphite cell housing and electrodes showed the first results of process feasibility.<sup>2</sup> The sulfide reaction mechanism was then explored in half-cell runs,<sup>3</sup> and further trials showed favorable kinetics for bench-scale runs.<sup>4</sup> NiO was shown to be a viable cathode material for polishing applications (*i.e.*, H<sub>2</sub>S levels below 60 ppm),<sup>5-7</sup> and optimum cell performance was modeled at low, intermediate, and high contamination levels.<sup>8</sup> Various membrane, electrode, and cell housing materials were tested in bench scale runs, but the choice of cathode material remains the major obstacle in scale-up.

The preferred reaction scheme is the following



This process selectively removes sulfur from the fuel gas while leaving only hydrogen behind to enrich the fuel stream. However, because of the large concentration of CO<sub>2</sub> and H<sub>2</sub>O relative to H<sub>2</sub>S at the cathode, a portion of the current goes toward the competing reactions below



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This competing reaction scheme results in hydrolysis and CO<sub>2</sub> transport instead of the intended transport of sulfur.

### Applications

Unlike adsorption and absorption methods for H<sub>2</sub>S removal,<sup>9,10</sup> an EMS would negate the need for both catalyst regeneration and stream reheating/cooling as long as high-temperature fuel cells or combustion turbines were employed. High-temperature molten carbonate and solid oxide fuel cells are also tolerant to CO and have shown resistance to slightly higher H<sub>2</sub>S levels (100 ppm) unlike proton exchange membranes.<sup>11,12</sup> But it is generally accepted that H<sub>2</sub>S levels have to be reduced below 1 ppm for even high-temperature fuel cells.

An EMS is appealing because the resulting fuel gas stream is both cleansed of the highly corrosive H<sub>2</sub>S as well as further enriched by H<sub>2</sub>. Elemental sulfur is the only sulfur by-product, which is benign (CO<sub>2</sub> may also be produced at the anode). Because the process is continuous, waste materials do not have to be handled and regenerated as in a sorbent method. This saves manpower and operating costs while avoiding exposure of personnel to potentially harmful materials. An efficiently designed cell stack may also ensure that the physical space required is minimal. In the coal industry, maintaining operation at temperatures at or above 600°C can theoretically cut the energy needs of an integrated gasification combined cycle (IGCC) process by approximately 20%. Additionally, the IGCC process offers reduction of CO<sub>2</sub> emissions by 35%.<sup>13</sup>

Based on economic estimates,<sup>5,10</sup> an H<sub>2</sub>S removal flux of 1.1 × 10<sup>-6</sup> gmol min<sup>-1</sup> cm<sup>-2</sup> would provide gas clean-up at a cost of \$0.32 per kilogram of H<sub>2</sub>S removed. With a contamination level of 1000 ppm H<sub>2</sub>S, a cell stack with 160 m<sup>2</sup> of active cell area could remove H<sub>2</sub>S at 1.0 g s<sup>-1</sup> from a gas flow of 4700 standard cubic feet per minute. Using square meter cells and limiting the thickness of each cell to at most 2 cm, the total volume of this EMS cell stack would be roughly 3.2 m<sup>3</sup>.

### Cathodes

*Cathode materials selection.*—A major hurdle that remains in process scale-up is cathode selection, as the lifetime of the cell depends heavily on the lifetime of the cathode material, which is exposed to sour gas. Simple sulfides, such as FeS, NiS, CuS, and MoS<sub>2</sub>, do not have adequate electrical conductivity and/or long-term stability because of their low melting points, solubility in the carbonate electrolyte, or poor reduction tolerance. Nb-doped TiO<sub>2</sub> has borderline electronic conductivity (0.01 S cm<sup>-1</sup> when 40% porous), reduction tolerance, and H<sub>2</sub>S tolerance, but it changes to a

nonconductive phase under the presence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at high temperature.<sup>14</sup> Mg-doped  $\text{LaCrO}_3$  and Sr-doped  $\text{LaCoO}_3$  and  $\text{LaGaO}_3$  have poor electrical conductivity ( $\ll 0.01 \text{ S cm}^{-1}$ ) in reductive environments, although their chemical stability in  $\text{H}_2\text{S}$  and  $\text{CO}_2$  atmospheres is good.  $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$  has good conductivity ( $\sim 200 \text{ S cm}^{-1}$ ), but it readily reacts with the sulfide electrolyte and  $\text{H}_2\text{S}$ , resulting in a compound with a low melting point. Because of these limitations in operating environment and temperature, other novel compounds were studied to find possible candidates for full-cell trials.

**Cobalt sulfide cathode.**—Under the operating conditions of this process, phase diagrams based on  $\text{H}_2\text{S}/\text{H}_2$  atmospheres predict that the pentlandite,  $\text{Co}_9\text{S}_8$ , is stable.<sup>15</sup> Past work has shown that  $\text{Co}_9\text{S}_8$  can be a stable phase, but questions still remain concerning its versatility in operating environment and preparation. Work by Weaver showed promise, reaching an  $\text{H}_2\text{S}$  removal flux of  $4.8 \times 10^{-6} \text{ mol min}^{-1} \text{ cm}^{-2}$  at  $650^\circ\text{C}$ .<sup>16</sup> His gas composition consisted of 41.0%  $\text{H}_2$ , 1.6%  $\text{CO}_2$ , 1.285%  $\text{H}_2\text{S}$ , 5.7%  $\text{CO}$ , and balance  $\text{N}_2$  after water-gas shift reaction. The membrane was composed of  $\text{LiAlO}_2$  and was 0.18 cm thick. Cell failure was attributed to gas crossover on account of density changes in the electrolyte upon sulfurization, resulting in membrane cracking.

Smith started with  $\text{LiCoO}_2$ , which was converted to  $\text{Co}_9\text{S}_8$  *in situ*.<sup>17</sup> He showed  $\text{H}_2\text{S}$  removal flux as high as  $1.9 \times 10^{-6} \text{ mol min}^{-1} \text{ cm}^{-2}$  at a fuel flow of  $328 \text{ mL min}^{-1}$ . The gas composition was 3.9%  $\text{H}_2$ , 2.85%  $\text{CO}_2$ , 0.61%  $\text{CO}$ , 8.14%  $\text{H}_2\text{O}$ , 2800 ppm  $\text{H}_2\text{S}$ , and balance  $\text{N}_2$  at  $650^\circ\text{C}$ . The Zircar prefabricated membranes used here were reportedly 69% porous and 0.062 cm thick. Failure was attributed to cathode pore flooding after excessive electrolyte had been added.

Although these results are promising, another issue is the preparation and optimized structure of this material. During sulfurization, a cobalt compound grows by outward diffusion of cations through the lattice, which is defected as a result of this movement. This phenomenon is capable of doubling the size of the initial pure cobalt sample. Although the rate of cation vacancy diffusion is independent of sulfur pressure, nonstoichiometry is a function of sulfur vapor pressure and is still being studied.<sup>18</sup> If a cobalt sulfide cathode is to be prepared *in situ*, its changes in volume and porosity upon sulfidation must be taken into account. The dependence of its structure and stoichiometry on  $\text{H}_2\text{S}$  vapor pressure must also be considered.

**Metal oxide cathodes.**—A selection of oxide materials were tested by Wang for conductivity and stability under sour conditions.<sup>19</sup> With a conductivity of  $15 \text{ S cm}^{-1}$ , it was determined that lithiated  $\text{Y}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  could be a viable cathode candidate. It was later tested in a full-cell run at  $650^\circ\text{C}$  under a gas composition of 3.7%  $\text{CO}_2$ , 25.8%  $\text{CO}$ , 4.6%  $\text{H}_2\text{O}$ , 65.6%  $\text{H}_2$ , and about 3000 ppm  $\text{H}_2\text{S}$ . The  $\text{H}_2\text{S}$  removal rate was  $1.1 \times 10^{-6} \text{ gmol cm}^{-2} \text{ min}^{-1}$  under an applied current density of  $75 \text{ mA cm}^{-2}$ . Lithiated  $\text{Y}_{1-x}\text{Ca}_x\text{FeO}_3$  was reported to have suitable performance in the working environment; it reacts with  $\text{H}_2\text{S}$  to form  $\text{FeS}$ ,  $\text{Y}_2\text{O}_2\text{S}$ , and  $\text{YFeO}_3$ , which are stable under the testing conditions.<sup>19</sup> However, the extended lifetime of this material is a concern, especially at higher temperatures.<sup>20</sup>

### Optimal Electrode Design

The electrodes need not only be chemically stable and conductive; they must also possess a structure idealized for gas transport to the electrolyte-electrode interface. Therefore, they must have porous structures that optimize this triple phase region. The electrode pores should be wetted with electrolyte but not flooded. From molten carbonate fuel cell studies, optimal electrode characteristics have been estimated to be a pore diam of 3–10  $\mu\text{m}$  and a thickness of 0.8–1 mm.<sup>21</sup>

Another problem is the preservation of this porous structure if a stable sulfide material is formed *in situ*. For example, pure cobalt

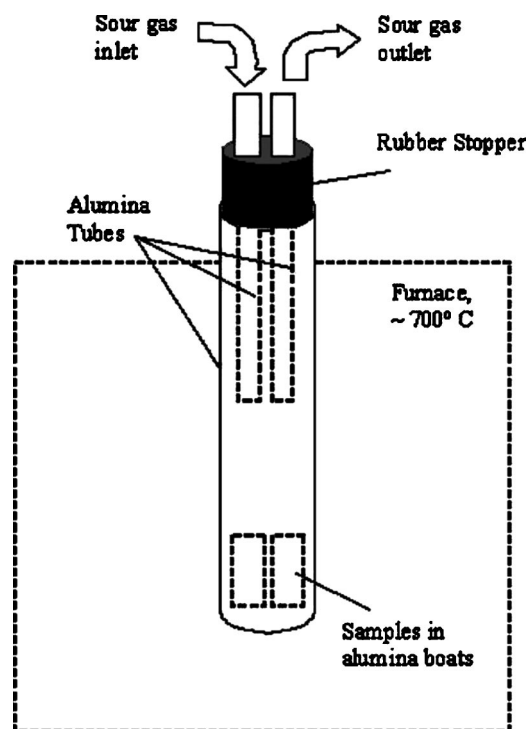


Figure 1. Diagram of stability run configuration.

has shown a volume increase upon formation of the  $\text{Co}_9\text{S}_8$  phase.<sup>22</sup> Care must be taken to preserve the optimal porous structure and wetting of the electrode. One way to accomplish this would be to start with an overly porous and thin electrode, which then sulfurizes to the optimal size and porosity upon reaction with  $\text{H}_2\text{S}$  and sulfide.

### Experimental

**Stability run setup.**—For the full-cell tests, an experimental setup was constructed that is capable of performing bench-scale EMS trials as described by Burke.<sup>20</sup> Likewise, the metal sulfide electrodes and the  $\text{Y}_{(0.9)}\text{Ca}_{(0.1)}\text{FeO}_3$  cathode were formed by the same methods used by Burke.<sup>20</sup>

For the chemical stability runs, a custom furnace and bubbler system was used to provide the operating environment. Each powder sample was put in an alumina boat, and up to four of these boats were tested at a time. The samples were placed in a 1 in. diam alumina tube, which was sealed at the top with a rubber stopper (see Fig. 1). Inlet and outlet gas tubes were poked through the rubber stopper, and vacuum grease was applied over all seals to prevent leakage. A good seal was verified by monitoring the outlet gas flow with a bubble meter.

The electrode materials  $\text{Sr}_2\text{FeMoO}_6$ ,  $\text{Sr}_2\text{CrMoO}_6$ ,  $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$  ( $x = 0.3$  and  $1.0$ ), and  $\text{Gd}_2\text{Ti}_{2-x}\text{Mo}_x\text{O}_7$  ( $x = 1.0$  and  $1.4$ ) were synthesized with a solid-state reaction method. The precursors are  $\text{SrCO}_3$  (Aldrich, 98%),  $\text{Gd}_2\text{O}_3$  (Alfa, 99.9%),  $\text{Fe}_2\text{O}_3$  (Aldrich, 99%),  $\text{Cr}_2\text{O}_3$  (Aldrich, 98%),  $\text{MoO}_3$  (Aldrich, 99.5%),  $\text{TiO}_2$  (Aldrich, 99.9%) and  $\text{V}_2\text{O}_5$  (Aldrich, 99.6%). Stoichiometric amounts of precursors were mixed thoroughly, pressed into pellets, and then heated in 4%  $\text{H}_2/\text{Ar}$  gas at  $1150^\circ\text{C}$  for 16 h. The pellets were ground, pressed into pellets, and heated for another 16 h.  $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$  ( $x = 0.3$ , and  $1.0$ ) was synthesized in pure  $\text{H}_2$  gas at  $1000^\circ\text{C}$  for 6 h X-ray diffraction (XRD) was used to check if the expected oxides were formed. For the stability tests, the oxide powders were mixed with the electrolyte ( $\text{Li}_{0.62}\text{K}_{0.38}\text{CO}_3$ ) in the volume ratio of 1:1 and then exposed to the syngas with 0.3%  $\text{H}_2\text{S}$  (40%  $\text{H}_2$ , 30%  $\text{CO}_2$ , 30%  $\text{CO}$ ) or 2.2%  $\text{H}_2\text{S}$  (60%  $\text{H}_2$ , 15%  $\text{CO}_2$ , 15%  $\text{CO}$ , and 8%  $\text{H}_2\text{O}$ ) at 700, 750, or  $800^\circ\text{C}$  for at least 40 h.

Upon exposure to H<sub>2</sub>S, the carbonate electrolyte becomes partially sulfide. The phase composition of each sample was checked by XRD.

**Conductivity samples.**—Rectangular bars cut from pressed pellets were used to measure the conductivity with an SI 1255 impedance analyzer in the frequency range of 100 Hz-5 MHz. Pt wires were connected to the end of the sample bars by Pt paste as the electrodes. The conductivity measurement was run in syngas with 0.3% H<sub>2</sub>S or in Ar with 4% H<sub>2</sub>. Scanning electron microscopy (SEM, Hitachi-S-800 microscope) was used to check the morphologies of the sample powders.

**Cathode material stability test.**—To expedite the search for possible cathode materials, stability tests were used to characterize chemical stability and conductivity under process conditions. Samples of potential cathode materials were exposed to sour fuel gas at 700-750°C for 2-3 days. In some cases, electrolyte was also added to the sample; the electrolyte was washed away in a water bath after the run. XRD analysis was used to determine whether or not each sample had changed phase and/or composition. The electrical conductivities of the materials were estimated under operating conditions (*i.e.*, sour gas at ~700°C) using a pressed pellet of the material.

**Evaluation of cathode performance.**—For promising cathode materials with good electrical conductivity and chemical stability, a bench-scale setup was used to evaluate electrode performance in full-cell runs. The cathode performance was registered in terms of continued removal flux of sulfur across the membrane and resistance to microstructure degradation. SEM analysis was used to analyze the morphology and microstructure of the cathode, and XRD was employed to check for changes in phase composition and crystal structure. H<sub>2</sub>S levels at the cathode and anode were monitored throughout the run to check for removal performance and gas crossover, respectively. CO<sub>2</sub> concentrations at the anode were also measured to observe the competing reaction of CO<sub>2</sub> transport.

## Results

**Stability results in full-cell runs for previously used cathode materials.**—The results with the cobalt sulfide electrode were discouraging because the electrode melted during operation. Smith<sup>17</sup> and Weaver<sup>16</sup> successfully used cobalt, sulfided *in situ*, but, in the most successful runs, a low CO<sub>2</sub> level was present in the fuel stream. The CO<sub>2</sub> concentration in this study was much higher than that used by Weaver and Smith; hence, Co<sub>9</sub>S<sub>8</sub> may not be stable under this gas phase. A possibility is that CoCO<sub>3</sub> was formed in the runs with high CO<sub>2</sub> and H<sub>2</sub>O levels. CoCO<sub>3</sub> is unstable at high temperatures and decomposes. But even temporary formation of this compound may induce degradation of the cobalt sulfide structure. This may account for the poor stability of cobalt sulfide in recent runs, even though postmortem XRD spectra reveal cobalt sulfide phases that should be stable above 700°C.

Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> has been used in multiple full-cell runs and has been very useful in acquiring data at 600-650°C. However, potential FeS absorption into the electrolyte and evidence of microstructural changes give reason to search for other materials. In a full-cell run at 700°C, a hole through the cathode material was slowly formed where the sour gas first makes contact with the cathode. This is strong evidence that this material cannot be used at this temperature.

**Stability runs.**—The materials in Table I were all tested for chemical stability in the cathodic operating environment. These oxides have high electrical conductivity (5-100 S cm<sup>-1</sup>) when they are partially reduced, but they needed to be tested under prolonged H<sub>2</sub>S and electrolyte exposure.

The stability and electrical conductivity of oxides with transition metals Mo, V, and Ti were investigated. Double perovskite oxides Sr<sub>2</sub>FeMoO<sub>6</sub> and Sr<sub>2</sub>CrMoO<sub>6</sub> have three-dimensional structures and

**Table I. Materials analyzed as possible cathode candidates**

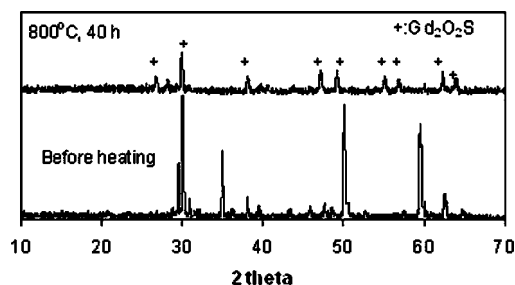
Perovskites	Pyrochlore	Others
(Single)	Gd <sub>2</sub> TiMoO <sub>7</sub>	BaLa <sub>2</sub> MnS <sub>5</sub> CoS <sub>2</sub> /LiCoO <sub>2</sub> Zn <sub>0.98</sub> Al <sub>0.02</sub> O CuIr <sub>2</sub> S <sub>4</sub> TiN
SrVO <sub>3</sub> La <sub>0.7</sub> Sr <sub>0.3</sub> VO <sub>3</sub> La <sub>1-x</sub> Sr <sub>x</sub> CrO <sub>3</sub> Sr <sub>2</sub> VO <sub>4</sub> Y <sub>0.9</sub> Ca <sub>0.1</sub> FeO <sub>3</sub> La <sub>0.9</sub> Sr <sub>0.1</sub> Ga <sub>0.8</sub> Cr <sub>0.2</sub> O <sub>3</sub> LaCr <sub>0.9</sub> Ti <sub>0.1</sub> O <sub>3</sub> SrCo <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>		
(Double)	SrFeMoO <sub>6</sub> Sr <sub>2</sub> CrMoO <sub>6</sub> BaLaMnMoO <sub>6</sub>	

Mo<sup>5+</sup> (d<sup>1</sup>) ions, so they both have high electronic conductivities. For example, Sr<sub>2</sub>FeMoO<sub>6</sub> is metallic, and its conductivity is 120 S cm<sup>-1</sup> at 27°C.<sup>23</sup> In reductive atmosphere at high temperatures, these oxides tend to lose some oxygen and reduce the valence of Mo to introduce more electrons into the conduction band, increasing electronic conductivity. All these oxides can be synthesized only in a highly reductive atmosphere, such as argon with 4-20% H<sub>2</sub> above 1000°C.<sup>24</sup>

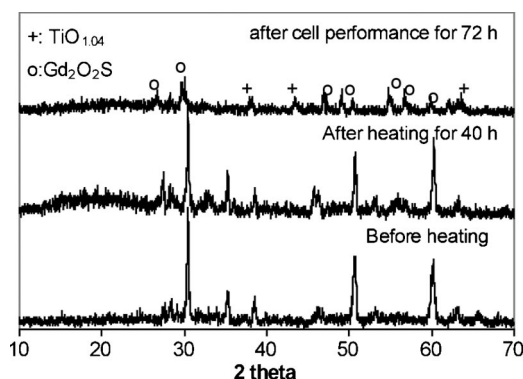
Oxides of the form Gd<sub>2</sub>Ti<sub>2-x</sub>Mo<sub>x</sub>O<sub>7</sub> (x = 0.0-2.0) with pyrochlore-type structure have been proposed as anode materials for fuel cells. They have high mixed ionic electronic conductivities (5-10 S cm<sup>-1</sup>) and good stability in a wide oxygen partial pressure range. Higher conductivity is present in the lower partial oxygen pressure atmosphere, which is good for application under fuel gas. In addition, Gd<sub>2</sub>Ti<sub>2-x</sub>Mo<sub>x</sub>O<sub>7</sub> oxides are synthesized in a mixed CO/CO<sub>2</sub> gas, thus showing CO<sub>2</sub> tolerance.<sup>25</sup>

Perovskite oxides with V<sup>3+/4+</sup> (d<sup>2</sup>/d<sup>1</sup>) ions are electrically conductive and stable in extremely reductive atmosphere.<sup>26-28</sup> For example, SrVO<sub>3</sub> is synthesized in pure H<sub>2</sub> at 1000°C, and its conductivity at 800°C is about 1000 S cm<sup>-1</sup>.<sup>26</sup> Considering the possibility that the electrodes may react with carbonate electrolyte under the operation conditions, the stability and conductivities of these oxides were examined with and without electrolyte while exposed to sour syngas.

**Promising novel cathode materials.**—Gd<sub>2</sub>Ti<sub>2-x</sub>Mo<sub>x</sub>O<sub>7</sub> (x = 1.4) mixed with electrolyte decomposed completely after being heated for 40 h in syngas with 0.3% H<sub>2</sub>S. The only phase that can be indexed from the XRD of the sample is Gd<sub>2</sub>O<sub>2</sub>S (Fig. 2). Because the stability of Gd<sub>2</sub>Ti<sub>2-x</sub>Mo<sub>x</sub>O<sub>7</sub> increases with increasing Ti content, we measured the performance of Gd<sub>2</sub>TiMoO<sub>7</sub> and found that there is no obvious change in the XRD spectra after it was heated for 40 h at 800°C (see Fig. 3). Its electrical conductivity in 4% H<sub>2</sub>/Ar is presented in Fig. 4. It is about 6 S cm<sup>-1</sup> at 650°C. A



**Figure 2.** XRD of Gd<sub>2</sub>Ti<sub>0.6</sub>Mo<sub>1.4</sub>O<sub>7</sub> immersed in electrolyte at 800°C for 40 h in syngas with 0.3% H<sub>2</sub>S.

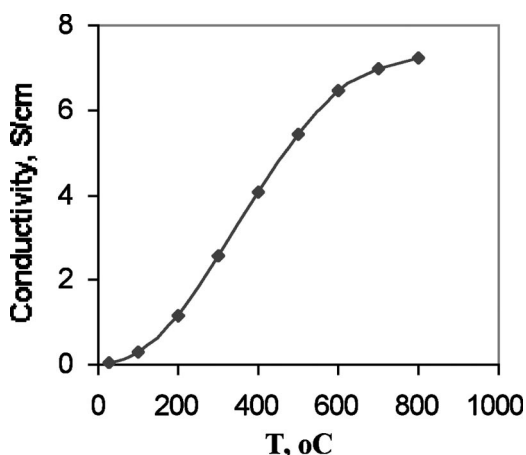


**Figure 3.** XRD of  $\text{Gd}_2\text{TiMoO}_7$  immersed in electrolyte at  $800^\circ\text{C}$  for 40 h in syngas with 0.3%  $\text{H}_2\text{S}$  and the sample after cell performance for 3 days.

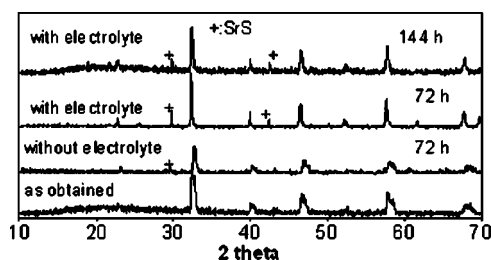
full-cell run tested the performance of  $\text{Gd}_2\text{TiMoO}_7$  as the cathode material. The feed gas for the test was syngas with 2.2%  $\text{H}_2\text{S}$ .  $\text{Gd}_2\text{TiMoO}_7$  decomposed to  $\text{Gd}_2\text{OS}_2$ ,  $\text{TiO}_{1.04}$ , and other phases after 4 days at  $650^\circ\text{C}$ . Because  $\text{TiO}_{1.04}$  has a high electrical conductivity ( $5000 \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ),<sup>29</sup> the composite derived from  $\text{Gd}_2\text{TiMoO}_7$  should also have adequate electrical conductivity. A previous report has confirmed that  $\text{TiO}_{1.04}$  has good  $\text{H}_2\text{S}$  tolerance;<sup>14</sup> hence, a  $\text{Gd}_2\text{TiMoO}_7$ -derived composite is a good cathode candidate for  $\text{H}_2\text{S}$  removal.

In another test, a small amount of SrS was indexed from the XRD spectra of a  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  sample after it was heated without electrolyte at  $750^\circ\text{C}$  in syngas with 2.2%  $\text{H}_2\text{S}$  for 72 h. When it was mixed with electrolyte in a 1/1 weight ratio and heated in syngas with 0.3%  $\text{H}_2\text{S}$  at  $750^\circ\text{C}$  for 72 h, no  $\text{LiVO}_2$  was indexed from its XRD, and only a small amount of SrS was found. No change was observed after the sample was heated for another 72 h under the same conditions (see Fig. 5). These facts indicate that, when electrolyte is present,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  has much better stability than  $\text{SrVO}_3$ . SEM showed that  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  did not melt at  $750^\circ\text{C}$  in the mixture with electrolyte for 6 days. The electrical conductivity of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  was measured in 4%  $\text{H}_2/\text{Ar}$  atmosphere; it is about  $30 \text{ S cm}^{-1}$  at  $650^\circ\text{C}$ .

$\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  is the most stable perovskite oxide with high electrical conductivity in an  $\text{H}_2\text{S}$ -containing atmosphere analyzed to date. Its stability increases with increasing La content, although its conductivity decreases. The low-Sr-containing members,  $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$  ( $x < 0.3$ ), are potential cathode materials for  $\text{H}_2\text{S}$



**Figure 4.** Electrical conductivity of  $\text{Gd}_2\text{TiMoO}_7$  in 4%  $\text{H}_2/\text{Ar}$ .



**Figure 5.** XRD of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  immersed in electrolyte at  $750^\circ\text{C}$  for 72 and 144 h.

removal.  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  did not melt in the stability runs and has an electrical conductivity of about  $20 \text{ S cm}^{-1}$  at  $650^\circ\text{C}$  under reducing gas.

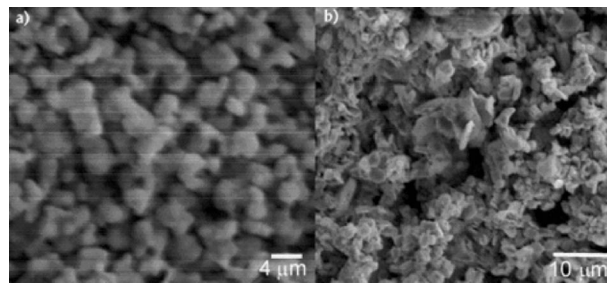
*Stability results in full-cell runs for novel cathode materials.*—For the materials that looked most promising in the stability trials, porous disks were prepared for use in full-cell runs. Cell performance was continually monitored, but even if there was gas crossover, the run was continued to observe the physical change of each cathode material in the working cell environment.

$\text{Gd}_2\text{TiMoO}_7$  showed resilience to pore deformation under the sour, reducing conditions. Figure 6 shows the SEM images of the cathode before and after a run at  $650^\circ\text{C}$  with 600 mA of current applied over its  $7.9 \text{ cm}^2$  surface. XRD revealed that the  $\text{Gd}_2\text{TiMoO}_7$ -derived composite converted to electrically conductive  $\text{TiO}_{1.04}$  and  $\text{Gd}_2\text{O}_2\text{S}$  with high melting point. It has good stability and a high electrical conductivity. Even though the composition changed, the pore structure appeared to be acceptable, signifying that the material may be made *in situ* without accounting for changes in volume and/or porosity. This material also achieved the highest removal rate achievable under the operating conditions ( $5.0 \times 10^{-7} \text{ gmol cm}^{-2} \text{ s}^{-1}$  at  $650^\circ\text{C}$  with a membrane 1.8 mm thick). A separate run at  $700^\circ\text{C}$  gave further support that this material has promising stability (see Fig. 7). The electrolyte side of the cathode showed a stable porous structure, but the side exposed to the gas had deformation, probably due to formation of  $\text{Gd}_2\text{O}_2\text{S}$ .

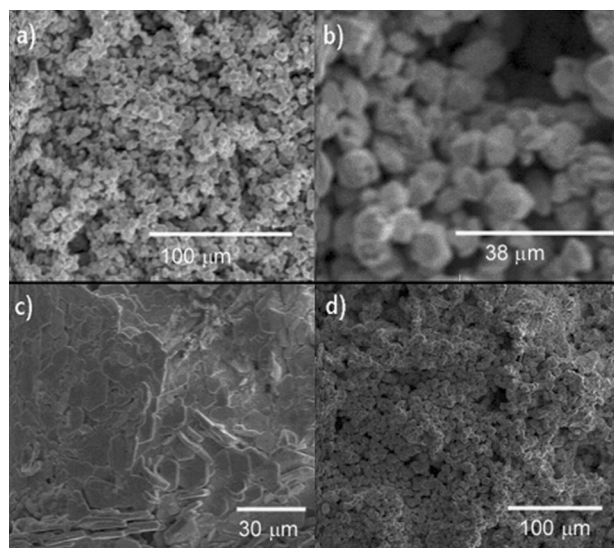
Due to membrane leakage in the cell,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  did not show good removal performance ( $2.0 \times 10^{-7} \text{ gmol cm}^{-2} \text{ s}^{-1}$  at  $700^\circ\text{C}$ ), but the XRD data show that this material kept its perovskite structure in this operating environment. However, in this XRD plot, there was much noise, possibly a result of polysulfide species formed. The SEM pictures in Fig. 8 show that the gas side of the cathode kept its porosity. The problem appears to be the side directly exposed to the electrolyte, in contrast to the case with  $\text{Gd}_2\text{TiMoO}_7$ .

## Discussion

*Sulfur binding energy.*—Recent studies in sulfide compounds and transition-metal oxides may help explain why certain materials performed better than others. Sulfur binding energy in transition

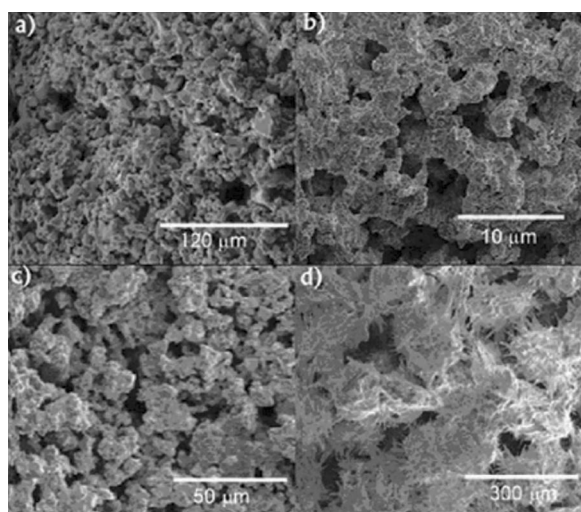


**Figure 6.** SEM images of  $\text{Gd}_2\text{TiMoO}_7$  (a) before and (b) after full-cell operation at  $650^\circ\text{C}$ . Note that pore structure is still intact.



**Figure 7.** SEM images of  $\text{Gd}_2\text{TiMoO}_7$  coated with  $\text{LiCoO}_2$  at  $700^\circ\text{C}$ . (a) standard, 1000 times, before run, (b) washed, 800 times, electrolyte side, after run, (c) washed, 700 times, gas side, after run, and (d) washed, 150 times, electrolyte side, after run.

metal sulfides has recently been related to catalytic activity in hydrotreating processes. Toulhoat *et al.* have shown that those materials with intermediate sulfur binding energies ( $45\text{--}60\text{ kcal mol}^{-1}$ ) have the highest catalytic activity.<sup>30</sup> In addition, mixtures of low and high sulfur binding energy compounds can produce a synergistic effect, resulting in the high catalytic activity seen in intermediate sulfur binding energy compounds. Cobalt, iron, and nickel all have low sulfur binding energy and exhibit metallic behavior. Mixing cobalt with molybdenum or nickel with tungsten can produce the synergistic effect, although the compound may inherit the semiconductive nature of the high sulfur binding energy metals. Low sulfur binding energy could be good for the EMS system, because that could allow sulfur ions to be released from the cathode surface more easily. The metallic nature is also preferable, as this would help decrease cell resistance.



**Figure 8.** SEM images of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  after use in full cell run. (a) standard, 1500 times, before run, (b) washed, 200 times, electrolyte side, (c) washed, 300 times, gas side, and (d)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  turned white upon exposure to oxygen, 100 times, electrolyte side.

*Novel oxide cathode materials.*—For perovskite-structured oxides, explanations for stability are based on resistance to sulfide formation. For  $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ , the trivalent lanthanum ion helps stabilize the compounds at low oxidant pressures or in the  $\text{H}_2\text{S}$ -containing atmosphere.<sup>26</sup> However, substituting strontium for lanthanum creates more defects in the lattice that increase the electrical conductivity of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$ .<sup>27,28</sup> A balance between conductivity and stability is achieved by the proper selection of the La/Sr ratio.

The electrical conductivity of  $\text{A}_2\text{B}_2\text{O}_7$  oxides with pyrochlore structures depends critically on the electronic structure of B cations and the oxygen vacancies in the lattice. In  $\text{Gd}_2\text{TiMoO}_7$ , it is the presence of molybdenum ( $\text{Mo}^{4+}, d^2$ ) that promotes conductivity by introducing conduction electrons.<sup>23,25</sup> However, after its structure changes upon exposure to  $\text{H}_2\text{S}$ , it appears that titanium oxide is responsible for the conductivity. SEM has shown that  $\text{Gd}_2\text{TiMoO}_7$  keeps its porosity despite this phase change (at least on the electrolyte side of the cathode). This means that a suitable cathode material may be made *in situ* by starting with a pyrochlore structure. More pyrochlore structures need to be analyzed to gain further insight into the resulting phases under sour operating conditions.

*Additional cell performance issues.*—Besides the development of a suitable cathode material, other issues must be addressed before this process can be most efficiently scaled up. Recent analysis of the yttria-stabilized zirconia membrane using quantitative microscopy has revealed that the pore structure is not optimized. The porosity is only 36% on average, much lower than the porosity of most molten carbonate fuel cell membranes (about 60%).<sup>31</sup> A more porous membrane would allow for higher sulfide fluxes, thus attaining higher  $\text{H}_2\text{S}$  removal rates. With an optimized membrane, sulfide diffusion across the membrane may no longer be the rate-limiting step, as the cell could possibly attain gas-phase diffusion limitations.

Some runs at 600 and  $650^\circ\text{C}$  failed due to gas crossover through the membrane. This was caused by cracks in the membrane and/or excessive loss of electrolyte. Once high sulfide levels are obtained in the electrolyte, solidification may occur, resulting in membrane cracking and gas crossover. Higher temperatures may be able to keep the electrolyte from solidifying; however, the electrode materials must be able to withstand these higher temperatures. Besides solidification, electrolyte loss due to evaporation may be another source of gas crossover.

## Conclusions

In the search for a suitable cathode material, more insight was gained into the stability of promising materials in a full-cell operating environment.  $\text{Li-Y}_{0.9}\text{CaFeO}_3$  and cobalt sulfide cathodes had limitations with regard to temperature and  $\text{CO}_2\text{--H}_2\text{O}$  levels, respectively. Among all metal oxides tested for stability in the sour operating environment,  $\text{Gd}_2\text{TiMoO}_7$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  appeared to be the best candidates. Each showed slight deformation in the full-cell operating environment, but these materials may be able to complement each other.  $\text{Gd}_2\text{TiMoO}_7$  appears to be stable under sour gas when the molten carbonate electrolyte is also present.  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$  is stable under pure sour gas but forms  $\text{SrS}$  when exposed to the molten carbonate. A layered electrode could offer a solution to this dilemma. An inner  $\text{Gd}_2\text{TiMoO}_7$  layer could be wetted by the electrolyte and protected from the sour gas by an outer layer of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$ . In this two-layer electrode, each material is shielding the other from the environment in which it is less stable. This possible synergistic effect merits further study for application in an EMS.

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