



# Ruthenium cluster-like chalcogenide as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells

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## ABSTRACT

This paper reports the incorporation of a cluster-like  $\text{Ru}_x\text{Se}_y$  as a methanol tolerant cathode catalyst in a laminar flow fuel cell. The effect on cell performance of several concentrations of methanol in the cathode stream was investigated for the  $\text{Ru}_x\text{Se}_y$  catalyst and compared to a conventional platinum catalyst. While the Pt catalyst exhibited up to  $\sim 80\%$  drop in power density, the  $\text{Ru}_x\text{Se}_y$  catalyst showed no decrease in performance when the cathode was exposed to methanol. At several methanol concentrations the  $\text{Ru}_x\text{Se}_y$  catalyst performed better than the Pt catalyst. This demonstration of a methanol tolerant catalyst in a laminar flow fuel cell opens up the way for further miniaturization of the cell design and simplification of its operation as the need for an electrolyte stream to prevent fuel crossover has been eliminated.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are of great interest as high energy density power sources because methanol has a higher energy density and is easier to store and transport than hydrogen. One of the challenges still hampering DMFC technology is methanol crossover: undesired transport to and electro-oxidation at the cathode leading to cross polarization and thus loss in overall fuel cell performance [1–5]. The occurrence of crossover limits the methanol concentration that can be used because higher concentrations lead to greater crossover. In laminar flow fuel cells (LFFC) as extensively studied by us [6–10] and others [11–16], the membrane present in most conventional fuel cell configurations is eliminated by exploiting the lack of turbulent mixing in microscale fluid flows [6–16]. The anode and cathode streams can be kept separated while flowing side-by-side in the same channel with the electrodes placed on opposing sidewalls. While fuel crossover can still occur due to slow diffusional mixing at the interface between the two streams, it can be minimized by control of the flow rates, minimizing the width of the fuel stream, and appropriate choice of electrode-to-electrode distance [6,8,12,16]. Still, a further decrease of fuel crossover is desired as it would enable further miniaturize

fuel cell designs and simplify their operation while increasing fuel utilization.

One approach to address the methanol crossover problem is the development of methanol tolerant catalysts for the oxygen reduction reaction (ORR). Pt and Pt-based alloys, the most widely used catalysts for the ORR, experience large decreases in performance in the presence of methanol. Many alternatives to Pt catalysts that are inactive towards methanol have been investigated, including metalloporphyrins [17–20], ruthenium chelates [21], various alloys [22–28], and metal chalcogenides [19,21,29–34]. In particular, Alonso-Vante et al. [29,35,36] as well as other researchers [19,30–33] have shown that ruthenium chalcogenide is tolerant to methanol while still very active for ORR. These catalysts have also been used as a selective cathode electrocatalysts in mixed-reactant fuel cells [37–39].

Here we study the use of ruthenium-selenium chalcogenides as a methanol tolerant cathode catalyst in a laminar flow fuel cell to eliminate the problem of fuel crossover thereby enabling further miniaturization in cell design and simplifying its operation.

## 2. Experimental

### 2.1. $\text{Ru}_x\text{Se}_y$ catalyst synthesis

$\text{Ru}_x\text{Se}_y$  was synthesized following previously reported procedures [40,41]. The characterization of the  $\text{Ru}_x\text{Se}_y$  was also reported in previous work [40,41].

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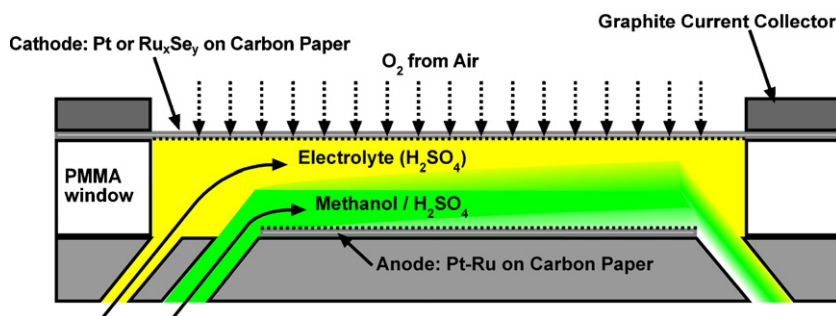


Fig. 1. Schematic diagram of an air-breathing laminar flow fuel cell (LFFC).

## 2.2. Fuel cell and electrodes

The design of the LFFC (shown in Fig. 1) and the preparation of the anodes and cathodes was the same as previously reported [9,10] with one minor modification. Instead of applying the anode catalyst directly to the graphite current collector plate, the catalyst was first applied to a gas diffusion electrode (GDE) and then clamped against the graphite backing. This modification improved the durability of the individual anode electrodes and allows electrodes to be changed easily while reusing all other parts of the cell. The channel in the cell is 3 mm wide and 3 cm long with an electrode area of  $0.54 \text{ cm}^2$  and spacing of 2 mm between electrodes. The anode catalyst consisted of  $10 \text{ mg/cm}^2$  Pt-Ru black (Alfa Aesar) with  $1.5 \text{ mg/cm}^2$  Nafion<sup>®</sup> on SGL 35 GDE. The two cathodes studied here were comprised of  $2 \text{ mg/cm}^2$  of either Pt black (Alfa Aesar) or  $\text{Ru}_x\text{Se}_y$  and  $0.1 \text{ mg/cm}^2$  Nafion<sup>®</sup> on an E-TEK "S" type GDE.

## 2.3. Catalyst testing

Each cathode was tested by operating the LFFC with two different cathode stream compositions. In all experiments, a  $0.5 \text{ M H}_2\text{SO}_4$  electrolyte solution containing 0.1, 1, 2, 5, 7, 10, or 15 M methanol was used as the anode stream. In the standard arrangement, the cathode stream was comprised of  $0.5 \text{ M H}_2\text{SO}_4$ . In the second arrangement, the cathode stream had the same composition as the anode stream, i.e. a certain [MeOH] in  $0.5 \text{ M H}_2\text{SO}_4$ . All streams each had a flow rate of  $0.3 \text{ mL/min}$ . For each case complete polarization curves were recorded at ambient conditions ( $21^\circ \text{C}$  and atmospheric pressure) using an in-house built test station and the individual electrode potentials were measured with a Ag/AgCl electrode as the reference electrode that is placed in the outlet stream as previously described [7,9,10]. The electrode potentials are not adjusted for IR.

## 3. Results and discussion

### 3.1. Pt cathode performance

Fig. 2a shows the polarization curves for the cell with a Pt cathode. For the experiments with a methanol stream on the anode side and an electrolyte stream that does not contain methanol on the cathode side (standard arrangement) the typical DMFC characteristics are observed (Fig. 2a1). At a methanol concentration of  $0.1 \text{ M}$  the performance is low due to mass transport limitations. As the concentration increases so does the performance until  $\sim 10 \text{ M}$ . At this point the performance peaks and begins to drop again. This phenomenon is due to either one or both of two effects. The first is the higher extent of fuel crossover to the cathode as the concentration increases. The other is the fact that methanol has a lower conductivity than water so the cell resistance increases with increasing methanol concentration, which decreases performance. The latter

is apparent in the experimental data from the noticeable decrease in the slope in the ohmic regime of the polarization curve (Fig. 2a1).

In the experiments where the electrolyte stream does contain methanol the cell's performance drops significantly (Fig. 2a2). The open circuit potential decreases by as much as  $0.39 \text{ V}$  from almost  $0.7 \text{ V}$  to less than  $0.3 \text{ V}$  and is indicative of mixed potentials and catalyst poisoning due to methanol oxidation on the cathode, well-known issues for membrane-based fuel cells such as DMFCs [1–5].

### 3.2. $\text{Ru}_x\text{Se}_y$ cathode performance

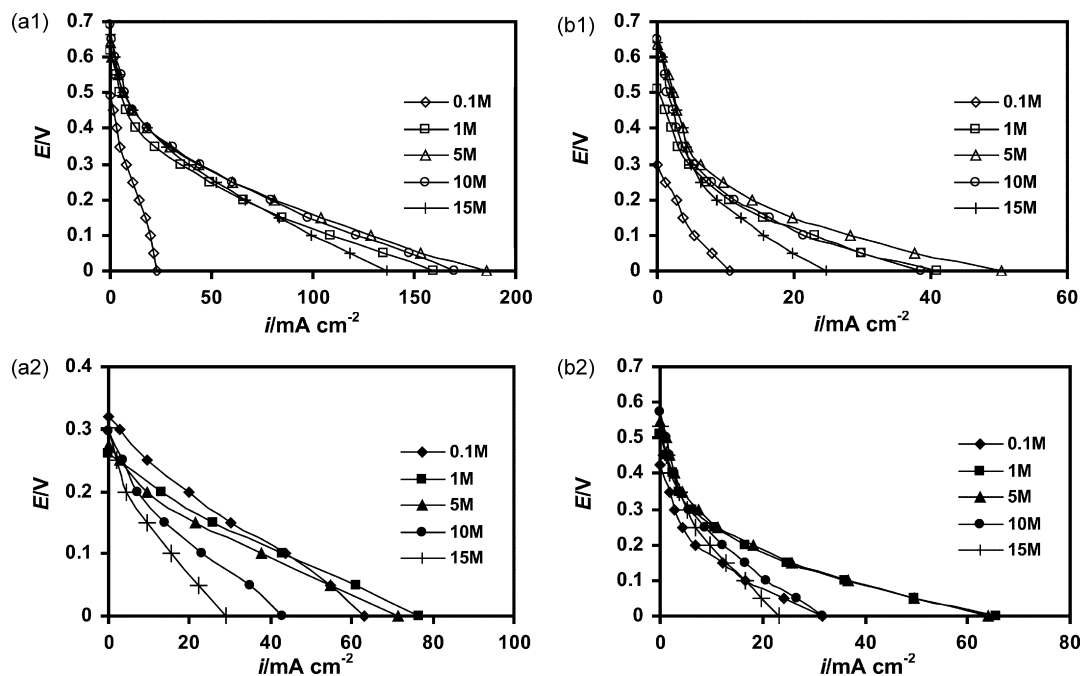
Fig. 2b shows the equivalent results when using a  $\text{Ru}_x\text{Se}_y$  instead of a Pt cathode. The polarization curves of the cell operated with the electrolyte stream without methanol (Fig. 2b1) are qualitatively similar to those for the Pt cathode (Fig. 2a1). The main difference is that the cell experiences larger losses in the kinetic region and achieves lower maximum current densities with the  $\text{Ru}_x\text{Se}_y$  catalyst ( $180 \text{ mA/cm}^2$  for Pt vs.  $50 \text{ mA/cm}^2$  for  $\text{Ru}_x\text{Se}_y$ ) confirming that  $\text{Ru}_x\text{Se}_y$  is not as active towards oxygen reduction as Pt [29,30,37]. However, contrary to the results seen for Pt (Fig. 2a2), when the  $\text{Ru}_x\text{Se}_y$  is used with methanol present in both the cathode and anode streams, no drop in performance occurs (Fig. 2b2) relative to the  $\text{Ru}_x\text{Se}_y$  cathode without methanol. Instead, a significant increase in performance is evident for almost all methanol concentrations, despite a small decrease in the open circuit potentials of less than  $0.1 \text{ V}$ .

### 3.3. Peak power densities

Table 1 lists the peak power densities for both cells with different cathode catalysts at each of the methanol concentrations for both experiments without and with methanol present in the electrolyte stream on the cathode side. With the exception of  $0.1 \text{ M}$ , in each case the Pt cathode exhibited a large decrease in performance, ranging from 67 to 88% when methanol was added to the cathode stream. With the  $\text{Ru}_x\text{Se}_y$  cathode, for all but the highest two methanol concentrations, the cell experienced significant increases in maximum power density, which ranged from 30 to more than 200%. A number of reasons could explain the increase in performance seen with the  $\text{Ru}_x\text{Se}_y$  cathode and the Pt cathode at  $0.1 \text{ M}$  methanol and are explored below. These results show that although Pt is a much better ORR catalyst in the absence of methanol,  $\text{Ru}_x\text{Se}_y$  performs better when the methanol concentration exceeds  $2 \text{ M}$  because of its methanol tolerance.

### 3.4. Individual electrode potentials

To further understand the differences in performance we analyzed the individual cathode and anode polarization curves (Fig. 3). These show the large drop in cathode potential for the Pt catalyst with methanol in the cathode stream (Fig. 3a2) compared



**Fig. 2.** Polarization curves of an air-breathing LFFC with (a) Pt and (b)  $\text{Ru}_x\text{Se}_y$  cathodes with methanol concentrations in the anode stream varying from 0.1 to 15 M. The cell was operated with a cathode stream comprised of (1) 0.5 M  $\text{H}_2\text{SO}_4$  and (2) 0.5 M  $\text{H}_2\text{SO}_4$  plus the same concentration of methanol as present in the anode stream. All data was collected at ambient temperature (21 °C) and pressure.

to experiments with an electrolyte stream without methanol (Fig. 3a1), which confirms the assumption that the losses occur because of mixed potentials from methanol on the cathode. No such drop occurs for the cell with a  $\text{Ru}_x\text{Se}_y$  cathode, but rather a small increase in performance is observed. This confirms previous findings [19,29–33,35,36] that the  $\text{Ru}_x\text{Se}_y$  catalyst is tolerant to methanol and does not experience the mixed potentials that occur with platinum.

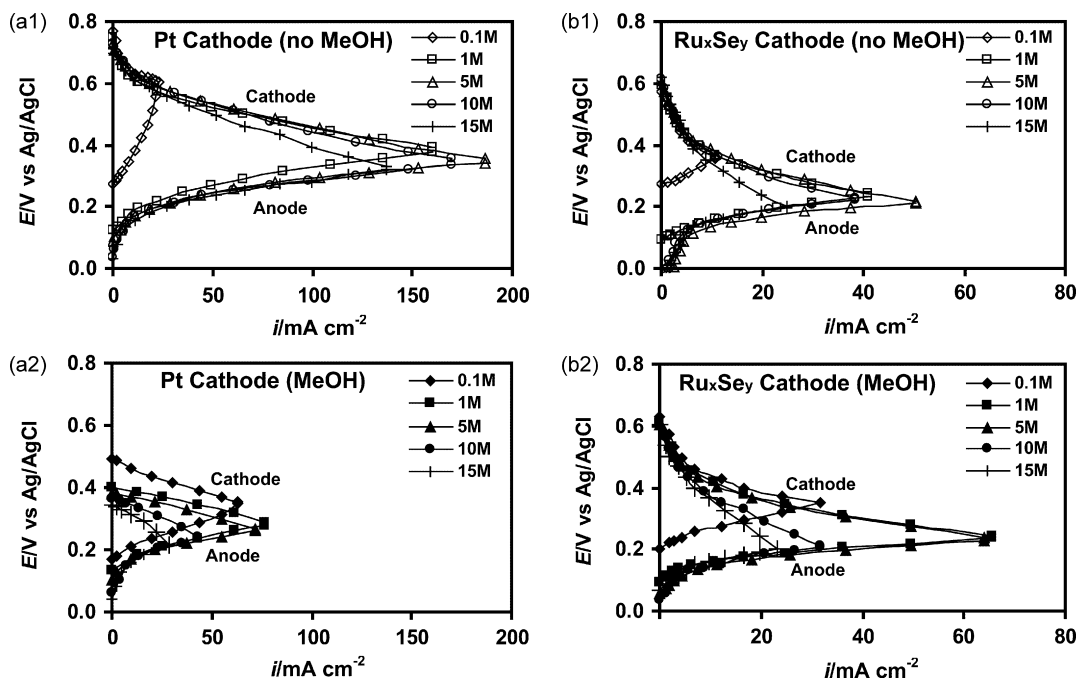
Fig. 3 also shows that when using either cathode catalyst the anode potentials are essentially the same for experiments performed with and without methanol in the cathode stream. The exception is the case of 0.1 M methanol concentration where the potential is significantly lower for the experiment with methanol on the cathode side. This indicates that insufficient mass transfer of methanol to the anode is not a factor in any of the experiments except the 0.1 M concentrations and thus is not the reason for the increase in performance seen for cell with a  $\text{Ru}_x\text{Se}_y$  cathode when methanol is added to the cathode side. Calculating the Peclet number ( $Pe$ ), a measure of the relative effects of convection and diffusion, further supports this [42]. For our experimental conditions  $Pe = 2000$  indicating that at the flow rate used the system is convection dominated and diffusion has a relatively small effect. Similarly the diffusion length of the methanol at the exit is calculated to be 0.19 mm, which is an order of magnitude smaller than the distance

between the electrodes. Hence, the anode will not even begin to feel the effects of methanol on the cathode side by the time the fluid exits, and thus cannot explain the increased performance.

Another possible explanation for the observed increase in performance when methanol is added to the cathode stream is that the methanol alters the transport properties of the oxygen, thus improving the cathode performance. The electrode potentials on the cathode exhibit an increase when methanol is present in the cathode stream (Fig. 3b), while, as mentioned before, the anode potentials are unchanged. This indicates that the performance increase is a result of effects on the cathode side and not the anode, which supports the hypothesis that changes in the solubility and diffusivity of oxygen are the cause of the increased performance. Itoe et al. showed that both the solubility and diffusivity of oxygen vary greatly with the methanol–sulfuric acid concentration ratio [43]. Their experiments showed that upon addition of methanol to 0.5 M sulfuric acid, the diffusivity of oxygen initially jumps by about a factor of 2.5–3 then steadily decreases until reaching the initial (methanol free) value at a concentration of several molar MeOH. The solubility shows the inverse behavior and initially decreases by a factor of 1.5–2 then increases reaching the original value at several molar MeOH. These combined effects on diffusivity and solubility as reported by Itoe et al. fully explain the results observed in our experiments. In particular it explains why the increases are greatest

**Table 1**  
Peak power densities of LFFCs with a Pt or  $\text{Ru}_x\text{Se}_y$  cathode, operated under operated with a cathode stream comprised of either (a) 0.5 M  $\text{H}_2\text{SO}_4$  «MeOH/SA» or (b) 0.5 M  $\text{H}_2\text{SO}_4$  plus the same concentration of methanol as present in the anode stream «MeOH/MeOH». All data was collected at ambient temperature (21 °C) and pressure.

[MeOH] (M)	Pt			RuSe		
	Peak power density (mW cm <sup>-2</sup> ) MeOH/SA	Peak power density (mW cm <sup>-2</sup> ) MeOH/MeOH	% Change w/MeOH added	Peak power density (mW cm <sup>-2</sup> ) MeOH/SA	Peak power density (mW cm <sup>-2</sup> ) MeOH/MeOH	% Change w/MeOH added
0.1	2.93	4.50	54%	0.56	1.83	230%
1	13.1	4.28	−67%	2.33	3.72	60%
2	14.8	4.28	−71%	2.72	4.00	47%
5	16.2	3.76	−77%	2.97	3.86	30%
7	15.9	3.69	−77%	2.83	3.72	31%
10	15.9	2.31	−85%	2.47	2.47	0%
15	13.3	1.56	−88%	1.83	1.94	6%



**Fig. 3.** Single electrode polarizations vs. Ag/AgCl for (a) Pt and (b)  $Ru_xSe_y$  cathodes operated with a cathode stream comprised of (1) 0.5 M  $H_2SO_4$  and (2) 0.5 M  $H_2SO_4$  plus the same concentration of methanol as present in the anode stream. All data was collected at ambient temperature (21 °C) and pressure. The potentials were not adjusted for IR.

at small methanol concentrations, where the diffusivity and solubility show the greatest change, while higher concentration show little or no change because the properties are approximately that of pure sulfuric acid. This also explains the improvement seen for the Pt cathode at 0.1 M, where the effects of methanol on the catalyst are small because of the low concentration, while the effects on oxygen transport are relatively large, leading to a net increase, which is smaller than that seen for  $Ru_xSe_y$ . This is quickly reversed when the methanol concentration increases because of the large negative effects of methanol on the Pt catalyst.

#### 4. Conclusions

This study demonstrates the incorporation of  $Ru_xSe_y$  as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells. The results presented here show that LFFCs with a  $Ru_xSe_y$  cathode outperform LFFCs with a Pt cathode when Methanol is present at concentrations as high as 15 M in the cathode stream. The  $Ru_xSe_y$  cathode performance actually *improves* in the presence of [MeOH], by as much as 30–60% at [MeOH] in the range of 1 to 7 M, compared to operation with no methanol present on the cathode side.

Despite the fact that the absolute performance of the cell with  $Ru_xSe_y$  cathode is a factor of 4 lower compared to the cell with Pt cathode ( $\sim 4$  mW/cm<sup>2</sup> vs.  $\sim 16$  mW/cm<sup>2</sup>), this disadvantage is outweighed by multiple advantages related to balance of plant (BOP) design, fuel cell stack configuration, and system operation. (i) Since fuel crossover is not a concern anymore, the electrolyte stream can be eliminated which eliminates the ancillaries to pump it, thereby decreasing the weight, size and complexity of the BOP. (ii) The electrode-to-electrode distance can now be minimized, which will reduce cell resistance resulting in an increase the performance of individual LFFCs, and more LFFCs will fit in a given volume, which will increase the specific energy of the fuel cell stack. (iii) A much higher fuel concentration can be used within the cell, potentially eliminating the need to dilute the fuel solution from a fuel cartridge. In summary, the implementation of a  $Ru_xSe_y$  cathode in

LFFCs greatly simplifies the overall system configuration, leading to a more compact and thus higher specific energy power source that is much simpler to operate.

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