



# Bi<sub>4</sub>Cu<sub>0.2</sub>V<sub>1.8</sub>O<sub>11-δ</sub> based electrolyte membrane reactor for selective oxidation of propane to acrylic acid

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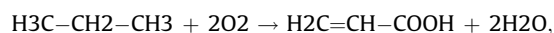
## ABSTRACT

An electrochemical membrane reactor using Bi<sub>4</sub>Cu<sub>0.2</sub>V<sub>1.8</sub>O<sub>11-δ</sub> as a solid electrolyte membrane was employed to investigate the selective oxidation of propane to acrylic acid over a MoV<sub>0.3</sub>Te<sub>0.17</sub>Nb<sub>0.12</sub>O catalyst. By applying an external current to the membrane reactor, the ionic oxygen was pumped to the surface of the MoV<sub>0.3</sub>Te<sub>0.17</sub>Nb<sub>0.12</sub>O catalyst, which exhibited higher conversion of propane and selectivity to acrylic acid than that in the fixed-bed reactor. The results indicate that the enhancement of catalytic performance in the membrane reactor is mainly due to the presence of the lattice oxygen, which has been proved to be necessary for the formation of acrylic acid. Thus, the Au/Bi<sub>4</sub>Cu<sub>0.2</sub>V<sub>1.8</sub>O<sub>11-δ</sub>/Au/MoVTeNbO membrane reactor achieved a higher conversion of propane (42%) and selectivity to acrylic acid (79.6%) at 380 °C with a 0.6 A current.

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## 1. Introduction

The selective oxidation of light alkanes into valuable products has attracted much interest in recent years [1]. In particular, the selective oxidation of propane to acrylic acid is one of the challenges with the objective of replacing the current 2-step propene to acrolein, then acrolein to acrylic acid process, since propane is much cheaper than propene. The most promising catalyst to date has been the MoVTeNbO system catalyst for the partial oxidation of propane to acrylic acid [2–5].



$$\Delta H = -171.2 \text{ kcal/mol}$$

For the selective oxidation of propane to acrylic acid, it has been found that the lattice oxygen from the MoVTeNbO catalyst plays an important role in increasing the catalytic activity [6]. Thus, the potential for enhancement of the acrylic acid yield appears to arise not only from catalyst improvement [7], but also by using the novel oxygen separation membrane reactors, which can continuously provide uniform and controllable lattice oxygen [8,9]. Different types of materials have been used in membrane reactors, but most of the membranes have appropriate oxygen conductivity at high temperatures (>800 °C) [10–16], which limits their application in

many selective oxidation reactions conducted at moderate or low temperatures (<500 °C). Fortunately, Abraham and co-workers found that Bi<sub>4</sub>Cu<sub>0.2</sub>V<sub>1.8</sub>O<sub>11-δ</sub> (known as BICUVOX.10) exhibits very high oxide ionic conductivity at low-to-moderate temperatures (300–600 °C) [17–20]. As the selective oxidation of propane to acrylic acid is carried out at approximately 400 °C, BICUVOX.10 is suitable as the solid electrolyte membrane reactor (SEMR) to provide the lattice oxygen in the selective oxidation of propane, in which air and hydrocarbon are fed to the cathodic and anodic chambers, respectively. Gaseous oxygen is reduced to O<sup>2-</sup> at the cathode, is transported through the electrolyte membrane to the anode, then reacts with the hydrocarbon on the catalyst surface and releases electrons. The released electrons are transported via an external circuit to the cathode and then reduce the oxygen again. The advantage of SEMRs is that the oxygen permeation rate can be directly controlled by the external current. When an external direct current was imposed between the anode and cathode, a stable and controllable oxygen anion flux was obtained. From the above, we conclude that the use of an SEMR gives a process in which oxygen as the lattice oxygen is supplied directly to the hydrocarbon, so the selectivity for the desired products might differ from those obtained in the fixed-bed reactor by directly supplying gaseous oxygen.

In the present paper, for the first time, the oxidation of propane to acrylic acid in the Bi<sub>4</sub>Cu<sub>0.2</sub>V<sub>1.8</sub>O<sub>11-δ</sub> membrane reactor combined with MoVTeNbO catalysts was investigated. The advantages of the SEMR over fixed-bed reactor for the selective oxidation of propane were explored by carrying out the reaction in both types of reactors under same reaction conditions.

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## 2. Experimental

### 2.1. Preparation of membranes and catalyst

BICUVOX.10 powders were prepared by both a solid-state reaction (SSR) method and an EDTA–citric acid (EC) process. For the SSR method, stoichiometric amounts of  $\text{Bi}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{CuO}$  were mixed and ground in an agate mortar. The resulting mixture was then successively heated to 500, 600 and 700 °C for 12 h, with a 20 °C/h heating/cooling rate. For the EC method [8,21], the required amounts of  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{NH}_4\text{VO}_3$  and  $\text{Cu}(\text{NO}_3)_2$  solution were added to EDTA–citric acid– $\text{NH}_3\cdot\text{H}_2\text{O}$  solution under heating and stirring. The mole ratio of EDTA, citric acid and total metal ions was controlled to be around 1:1.5:1. Ammonia was used to adjust the pH value close to 6 to keep the solution transparent during the whole process. After the water was evaporated, the resulting blue gel was treated at 400 °C to remove the organic compounds. The powder was then successively calcined at 500, 600 and 650 °C for 12 h with a 20 °C/h heating/cooling rate. The phase structures of the as-prepared powders were determined by X-ray diffraction (XRD, Rigaku D/Max-2500, Cu K $\alpha$ ). The BICUVOX.10 powders obtained from the two methods were pressed into disks 18 mm in diameter, and sintered at 700–800 °C for 2 h with a heating and cooling rate of 3 °C/min. The surface morphologies of the membranes were observed using a Quanta 200F scanning electron microscopy (SEM).

The  $\text{MoV}_{0.3}\text{Te}_{0.17}\text{Nb}_{0.12}\text{O}$  catalyst (denoted as MoVTeNbO) was prepared by the hydrothermal method, which has been reported in detail in the literature [22]. Firstly, 5.35 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and 1.16 g  $\text{H}_6\text{TeO}_6$  were dissolved in 20 ml water at 80 °C. A second solution was prepared by dissolving 2.37 g  $\text{VOSO}_4\cdot n\text{H}_2\text{O}$  in 10 ml water. The third solution was prepared by dissolving 2.33 g  $\text{Nb}_2(\text{C}_2\text{O}_4)_5\cdot n\text{H}_2\text{O}$  in 10 ml water at 80 °C. Then the second solution was added to the solution containing molybdenum and tellurium and the resulted mixture was stirred for 5 min. After that, the third solution was put into the mixture and stirred for 10 min at 80 °C before being introduced into the autoclave. After 5 min  $\text{N}_2$  bubbling, the autoclave was heated to 175 °C for 48 h. The slurry obtained was filtered and dried at 80 °C for 12 h and then calcined

under  $\text{N}_2$  at 600 °C for 2 h. Finally the MoVTeNbO sample was crushed and sieved to retain particles with 40–60 mesh diameter. The total conductivity of the catalyst was measured using a bar-shaped sample (10 mm  $\times$  4 mm  $\times$  2 mm) in the atmosphere of propane diluted by  $\text{N}_2$  at 380 °C with a four-probe method using a Keithley 2000 multimeter and potentiostat (Princeton Applied Research 263A). The concentration of propane is 10%.

### 2.2. Electrochemical separation of oxygen

A BICUVOX.10 membrane reactor (Fig. 1) was designed for the separation of oxygen and the oxidation of propane. All of the membrane disks were polished to 1.2 mm in thickness. Gold paste was brushed on to both sides of the pellet to act as electrodes and treated at 650 °C for 1 h. The effective membrane areas were controlled to around 1.0 cm<sup>2</sup>. The pellet was then sealed into the steel tube (13 mm inner diameter) using phosphate-based refractory cement. Gold wires were pressed against the two sides of the pellet by means of an adjustable spring to conduct electrons. The driving current was supplied by the potentiostat (Princeton 263A). He (50 ml/min) and air (50 ml/min) were introduced into the anodic and cathodic chambers, respectively. The oxygen permeation rate was analyzed by a gas chromatograph (GC, Agilent 6890). The theoretical oxygen permeation can be calculated by the Faradic law and the ratio of experimental oxygen flux to the theoretical value is defined as the Faradic efficiency.

### 2.3. Selective oxidation of propane to acrylic acid in SEMR

The anodic layer of the SEMR serves both as an electrode and as a catalytic zone for the desired selective oxidation. Its design has a critical effect on the reactor performance. Accordingly, as shown in Fig. 1, the SEMR was designed in two modes according to the different packing of the MoVTeNbO catalyst in the electrochemical reactor. (1) The anodic layer serves only as an electrode. Au paste was applied as both cathode and anode metal on two sides of the BICUVOX.10 disc, and 2 g MoVTeNbO catalyst were packed on to the catalytically inactive anode. The SEMR obtained is denoted as Au/BICUVOX.10/Au/MoVTeNbO (Fig. 1a), and the applied current

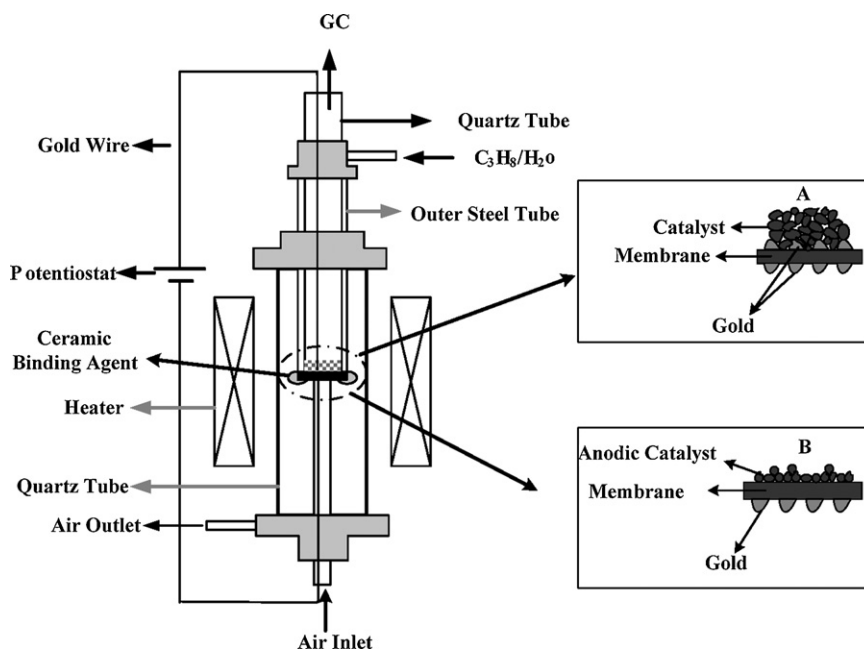


Fig. 1. Solid electrolyte membrane reactor for oxygen separation and selective oxidation of propane to acrylic acid. (A) Schematic diagram showing the catalyst packed on Au layer. (B) Schematic diagram showing catalyst pasted directly on to the membrane as an anodic catalyst.

increased from 0.2 to 0.8 A. (2) The cathode is still made by Au paste. MoVTeNbO paste was applied as anode and catalyst on to the other surface of the BICUVOX.10 disc. At this case, 50 mg MoVTeNbO catalyst was ground up with glycol and then pasted to the anodic side of the membrane followed by heating at 400 °C for 2 h to eliminate the glycol. This configuration is denoted as Au/BICUVOX.10/MoVTeNbO (Fig. 1b), and the applied current was adjusted from 0.01 to 0.06 A. In both modes, the operating temperature was 380 °C. The flow rate of air to the cathodic chamber was 50 ml/min. The flow rates of propane and water vapor to the anodic chamber were 1 and 12 ml/min, respectively, and the mixture of propane and water vapor was diluted by helium to keep the total flow rate 28 ml/min.

To check the effect of gaseous oxygen, the selective oxidation reaction of propane was carried out in a conventional fixed-bed quartz tubular reactor at atmospheric pressure at 380 °C. 2 g MoVTeNbO catalyst was introduced into the reactor and the feed composition was kept at  $C_3H_8:H_2O(gas):(O_2 + He) = 1:12:15$  by adjusting the oxygen and helium flow rates simultaneously. The gaseous oxygen was varied from 1.5 to 3 ml/min.

The blank reactor with Au/BICUVOX.10/Au in the absence of MoVTeNbO catalyst was tested under similar conditions to that with the MoVTeNbO catalyst. Under an imposed current from 0.2 to 0.8 A, only traces of  $CO_2$ ,  $C_2H_4$  and  $C_2H_6$  were detected and the amounts were negligible compared to those obtained in the reactor with the MoVTeNbO catalyst.

The liquid products were collected with cold water and analyzed by GC (Agilent 6890) equipped with FID and the gas products were analyzed with a TCD.

### 3. Results and discussion

#### 3.1. Structures and morphologies of the membrane

Fig. 2 shows the X-ray diffraction patterns of the BICUVOX.10 powders synthesized by the EC process (Fig. 2A) and SSR method (Fig. 2B) as a function of the calcination temperature. Fig. 2A shows no obvious change with temperature for BICUVOX.10 powder synthesized by the EC method up to around 600 °C at which an undesirable phase appears. This phase can be satisfactorily ascribed as  $BiVO_4$  [23]. A further increase in temperature leads to the appearance of a desirable orthorhombic BICUVOX phase at around 650 °C. In contrast, for the BICUVOX.10 powder synthesized by the SSR method, the desired crystallographic phase was fully developed until the temperature reached 800 °C (Fig. 2B), which is close to the melting point of the membrane. Below 800 °C, the XRD patterns differ somewhat from those observed for the material by the EC method, showing the absence of a  $Bi_2O_3$  phase. This suggests that the difference in temperature at which the orthorhombic BICUVOX structure appeared with the different preparation methods.

SEM measurements were carried out to study the morphologies of BICUVOX.10 membranes. Typical surface and cross-sectional SEM images of membranes synthesized by the SSR and EC methods with sintering at 800 °C for 2 h are shown in Fig. 2. It is clear from the SEM images that ceramic grains with clear boundaries are densely packed together, and the grain size of the membrane from the EC method is much larger than that from the SSR method, indicating that a directional grain growth took place (Fig. 3A) for the membrane derived from the EC process. Although the membranes appear dense from the top, there are many closed pores in the cross-sections of the membranes prepared with both methods. It is important to note that the closed pores in the membrane from SSR are larger than those in the membrane from EC. This could be due to the larger initial particle size of the powder from the SSR method.

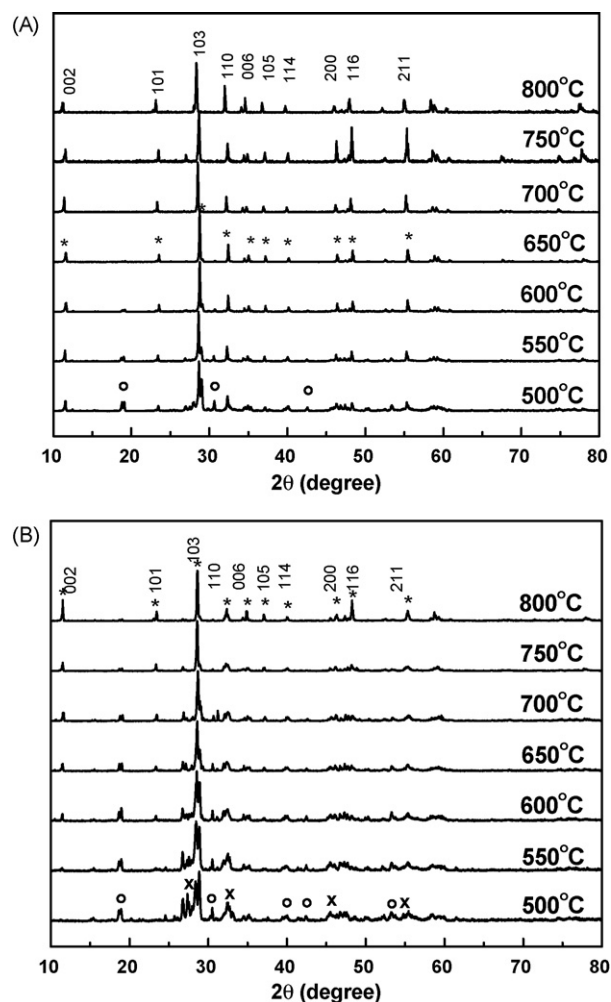


Fig. 2. XRD patterns of BICUVOX.10 oxide powders synthesized by (A) the EC method and (B) the SSR method at different temperatures. The main diffraction peaks of BICUVOX.10 (\*),  $BiVO_4$  (○) and  $Bi_2O_3$  (×) are shown.

#### 3.2. Oxygen permeation performance of membranes derived from EC and SSR method

In order to investigate the ability of BICUVOX.10 membranes prepared using different synthetic methods to separate oxygen gas, a series of oxygen permeation tests were performed at 400 °C on BICUVOX.10 membranes synthesized by the EC and SSR methods, with optimized sintering temperatures of 700 °C and 800 °C, respectively. As shown in Fig. 4, it was apparent that the BICUVOX.10 membrane prepared from the SSR method was more stable than that from the EC method. This result shows that the preparation method played an important role in the oxygen permeation performance of the BICUVOX.10 membrane. For the membrane from the EC method, when the applied current was higher than 0.8 A, the Faradic efficiency decreased dramatically and was accompanied by a significant decline in the oxygen permeation (Fig. 4A). However, for membranes prepared with the SSR method, it is important to note that the Faradic efficiency was above 80% over the entire current intensity range studied. In particular, the volume of oxygen transferred by the membrane was strictly proportional to the current density (Fig. 4B). From the report by Boivin and co-workers [19], it is known that, at low current density, the oxygen molecules are dissociated in the usual way at the triple point boundary within the gold grid, the electrolyte and the gas phase. With increase of current density, the number of triple points becomes too small and a partial reduction

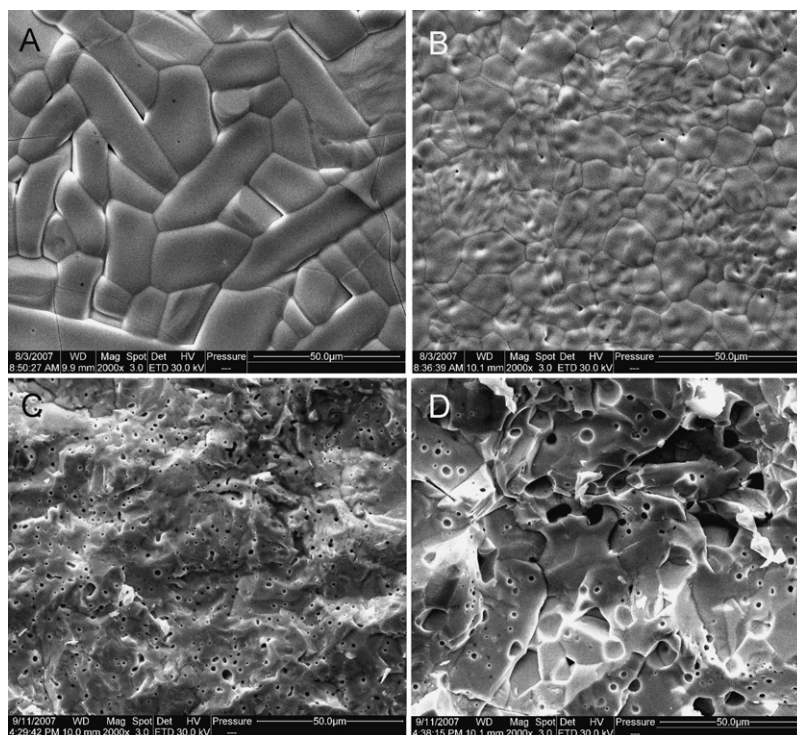


Fig. 3. SEM images of as-prepared membranes synthesized by the EC (A and C) and SSR (B and D) methods. (A and B) top view; (C and D) cross-section.

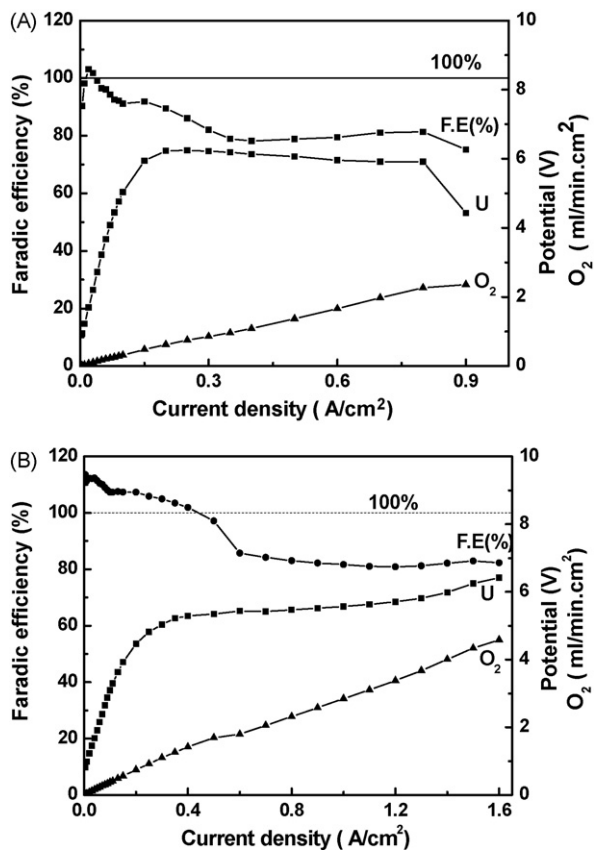


Fig. 4. Electrical characteristics for the BICUVOX.10 membranes operating at 400 °C. (A) synthesized by EC method (B) synthesized by the SSR method.

of the membrane occurs without significant structural changes. As a consequence, the oxygen permeation rate and the Faradic efficiency sharply decreased. Based on this rule, we think that the high stability of the membrane prepared using the SSR method is related to the crystallization (Fig. 2) and morphology (Fig. 3) of the membrane, which makes it possible to have higher stability when the current density was increased. Further investigations are required to detail the explanation.

The oxygen permeation studies carried out with a range of current densities revealed that the membrane prepared with the SSR method is more suitable for the construction of the membrane reactor for the propane oxidation reaction, since a very precise and quantitative control of oxygen flux can be obtained by adjusting the applied current.

### 3.3. The effect of the oxygen pumping on selective oxidation of propane

The catalytic performance of Mo-V-Te-Nb-O catalysts in both a fixed-bed reactor and a membrane reactor are shown in Table 1. Acrylic acid, propene, acetic acid and carbon oxides were the main reaction products although a little ethylene, ethane, acetone were also observed. It can be found that the catalytic performance is strongly dependent on the oxygen content. In the fixed-bed reactor, the conversion of propane increased with increasing the flow rate of oxygen, which means that the higher oxygen concentration is favorable for propane activation. But for the selectivity to acrylic acid, a maximum selectivity (73.0%) is observed for 1.8 ml/min of oxygen flow rate. It is well known that the theoretical  $V(O_2)/V(C_3H_8)$  ratio equals to 2, when the oxygen concentration is above this ratio, acrylic acid and other intermediates, including propene and acetic acid, have a tendency to be over-oxidized to  $CO_x$ , in which a sharp increase in the



**Table 1**

The catalytic performance for Au/BICUVOX.10/Au/MoVTeNbO membrane reactor (SEMR) and fixed-bed reactor at 380 °C. The loaded catalysts in both reactors were 2 g. C<sub>3</sub>H<sub>8</sub> 1 ml/min, H<sub>2</sub>O vapor: 12 ml/min, Helium was adjusted with the oxygen flow rate (or current) to keep the total flow to about 28 ml/min.

Reactor	Oxygen or current	Conversion (%)	Selectivity (%)					AA Y (%)	AA rate g/(g min)
			AA	CO <sub>x</sub>	C <sub>3</sub> H <sub>6</sub>	AcA	Oth.		
SEMR	0.2 A (0.7 ml/min)	20.0	75.3	8.6	6.2	4.7	5.2	15.0	0.24
	0.4 A (1.2 ml/min)	28.8	78	9.8	3.4	6.6	2.2	22.5	0.37
	0.6 A (1.8 ml/min)	42.0	79.6	10.0	3.0	7.2	0.2	33.4	0.54
	0.8 A (2.4 ml/min)	49.4	73.0	14.6	2.9	8.4	1.1	36.0	0.59
Fixed bed reactor	0.7 ml/min	19.7	69.0	9.0	8.8	8.2	5.0	13.6	0.22
	1.2 ml/min	28.0	72.4	9.5	7.3	6.9	3.9	20.3	0.33
	1.8 ml/min	36.1	73.0	10.2	6.6	7.0	3.2	26.4	0.43
	2.4 ml/min	39.2	71.3	14.6	5.3	6.8	2.0	27.9	0.46

AA: acrylic acid; AcA; Oth.: C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> + CH<sub>4</sub> + acetone.

selectivity to CO is observed. In SEMR of Au/BICUVOX.10/Au/MoVTeNbO, oxygen was pumped to anode and the permeation rate varied from 0.7 to 2.4 ml/min with varying the applied current from 0.2 to 0.8 A. It is obvious that the changing tendency in the conversion of propane and the selectivity to the products is similar to those in the fixed-bed reactor. But the selective oxidation of propane was rather enhanced under oxygen pumping compared with the results obtained by gaseous oxygen, for example, the yield of acrylic acid in SEMR was up to 36% which is much higher than that in the fixed-bed reactor (27.9%) with same oxygen flow rate of 2.4 ml/min, as shown in Table 1. This fact is clearly demonstrated that the membrane configuration alters the reaction environment, which can have a significant effect on the yield of acrylic acid.

It is well-documented that the surface oxygen species are usually relevant to the catalytic performance. In the fixed-bed reactor, the adsorbed oxygen species on the MoVTeNbO catalyst are relevant to gaseous oxygen. But in the membrane reactor, the high oxygen-ion conductivity of BICUVOX.10 membrane is associated with its high property to supply electrochemically the lattice oxygen, which can be used to promote the selective oxidation of the alkane. Furthermore, according to the literature from Ueda et al. [22], it was also suggested that the C<sub>3</sub>H<sub>8</sub> activation preferentially takes place on the surface lattice oxygen in the MoVTeNbO catalyst. Accordingly, for the Au/BICUVOX.10/Au/MoVTeNbO membrane reactor, as current was imposed, one part of the lattice oxygen was supplied to the catalyst surface contacting the membrane, in which it could provide excellent conversion of propane and higher selectivity to acrylic acid than in the fixed-bed reactor. And it is inevitable that the other part of the lattice oxygen recombined to molecular oxygen again. Meanwhile, with the increase in the current, the concentration of the lattice oxygen O<sup>2-</sup> on catalyst surface increased, in which a further increase in the conversion of propane and selectivity to acrylic acid was observed. But when the applied current increased to some extent (0.8 A), more and more lattice oxygen recombined to molecular oxygen and was released as

gaseous oxygen, which is responsible for the significant decrease in the selectivity to acrylic acid. Especially, in this case, it is obvious that the selectivity to acrylic acid is quite similar for the membrane reactor and the fixed-bed reactor.

From above, it can be noted that, in the Au/BICUVOX.10/Au/MoVTeNbO reactor, due to the gold layer locating between the membrane and the catalyst, the MoVTeNbO catalyst was difficult to fully touch the membrane. Since the MoVTeNbO catalyst has enough conductivity, in order to further investigate the important effect of the lattice oxygen on the catalytic performance, 50 mg MoVTeNbO catalyst paste was directly brushed to the membrane as anodic catalyst in the Au/BICUVOX.10/MoVTeNbO membrane reactor and the catalytic results are shown in Table 2. It was found that the conductivity of the MoVTeNbO catalyst was about 3.2 s/cm at 380 °C tested by the four-probe method, which made it possible to replace Au as anode and ensured that the electrochemical process carried on the Au/BICUVOX.10/MoVTeNbO membrane. It was revealed that the direct application of the lattice oxygen to the whole MoVTeNbO catalyst surface appeared to favor the selective formation of acrylic acid, in which approximately 86% of selectivity was obtained and kept at this level in the whole range of the imposed current. This further confirmed that the lattice oxygen ions on the surface of the catalyst play important roles in selectivity of acrylic acid. To make sure the role of the oxygen pumping (or the lattice oxygen) in the reaction, the gaseous oxygen was co-fed to the anode side under open circuit. It is noticeable from Table 2 that, with the application of gaseous oxygen, the conversion of propane and selectivity to acrylic acid was significantly decreased. Especially, on the anodic MoVTeNbO catalyst with oxygen pumping, very high formation rate of acrylic acid (1.82 g/(g-cat min)) was obtained. In general, when current is imposed, the anodic MoVTeNbO catalyst serves as both electrode and catalyst for the selective oxidation reaction. So it is possible to achieve high yields of the desired product in SEMR by a single anodic electrode material, which possesses high conductivity and good catalytic properties for the catalytic reaction. In our case,

**Table 2**

The catalytic results for Au/BICUVOX.10/MoVTeNbO membrane reactor under closed and open circuit conditions at 380 °C. The loaded catalysts were 50 mg. C<sub>3</sub>H<sub>8</sub> 1 ml/min, H<sub>2</sub>O vapor: 12 ml/min, Helium was adjusted with the oxygen flow rate (or current) to keep the total flow to about 28 ml/min.

Reactor	Oxygen or current	Conversion (%)	Selectivity (%)				AA Y (%)	AA rate g/(g min)
			AA	C <sub>3</sub> H <sub>6</sub>	CO <sub>x</sub>	Oth.		
SEMR	0.01 A (0.04 ml/min)	1.2	85.0	–	13.0	2.0	1.0	0.65
	0.02 A (0.08 ml/min)	1.8	86.0	–	13.2	0.8	1.5	0.97
	0.04 A (0.16 ml/min)	2.6	86.2	–	13.5	0.3	2.2	1.43
	0.06 A (0.2 ml/min)	3.3	86.0	–	13.4	0.6	2.8	1.82
SEMR open circuit	0.13 ml/min	1.4	79.5	6.7	12.1	1.7	1.1	0.71
	0.16 ml/min	1.6	79.0	6.9	12.8	1.3	1.3	0.85
	0.19 ml/min	1.8	79.8	6.8	13.0	0.4	1.4	0.92

AA: Acrylic acid; Oth.: C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> + CH<sub>4</sub> + acetone.

the combination of anodic MoVTeNbO catalyst and BICUVOX.10 electrolyte membrane makes it an attractive reactor design to exhibit excellent catalytic performance in the selective oxidation of propane to acrylic acid.

#### 4. Conclusion

The Au/BICUVOX.10/Au/MoVTeNbO and Au/BICUVOX.10/MoVTeNbO membrane reactors were successfully designed and showed a better catalytic performance in the selective oxidation reaction of propane to acrylic acid compared to the fixed-bed reactor. Stable and controllable lattice oxygen, which was responsible for the enhancement of catalytic performance, was continuously obtained at moderate temperatures by applying a direct current for the SEMR. The results proved that the electrochemical membrane reactor has the potential applications in the selective oxidation of alkanes.

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