

令和 5 年 5 月 26 日現在

機関番号：17102  
 研究種目：研究活動スタート支援  
 研究期間：2021～2022  
 課題番号：21K20490  
 研究課題名(和文) Development of next generation proton-conducting solid oxide cells (P-SOC) towards environment-friendly power-to-X (PtX) reactions  
 研究課題名(英文) Development of next generation proton-conducting solid oxide cells (P-SOC) towards environment-friendly power-to-X (PtX) reactions  
 研究代表者  
 SHI NAI (SHI, NAI)  
 九州大学・エネルギー研究教育機構・学術研究員  
 研究者番号：10906217  
 交付決定額(研究期間全体)：(直接経費) 2,300,000円

研究成果の概要(和文)：本研究では、プロトン伝導性酸化物を用いた大面積膜型反応器(P-SOC)を構築し、Pt/Nb<sub>2</sub>O<sub>5</sub>触媒をセルに担持した電気化学的プロパン脱水素化反応を実証した。膜型反応器への電圧を印加は、アノードのプロパン脱水素化反応とカソードのCO<sub>2</sub>還元を促進し、300℃において100時間安定に動作することが分かった。反応中間体評価によりプロパン解離が速度制限段階であることがわかった。

#### 研究成果の学術的意義や社会的意義

This work is the first trail to realize olefin production using P-SOC at a low temperature of 300 oC, we also obtained remarkable electrochemical performance comparing to reported literature results. This work should pave a new way for the chemical synthesis.

研究成果の概要(英文)：Overall, we have accomplished the proposed targets listed below (1) We have successfully fabricated 2 P-SOC configurations with effective area ranging from 0.5~12 cm<sup>2</sup>. (2) The Pt/Nb<sub>2</sub>O<sub>5</sub> catalyst was found to be suitable for propane dehydrogenation in P-SOCs. (3) External electricity promotes propane dehydrogenation and CO<sub>2</sub> reduction, as confirmed by on-line GC and mass spectroscopy. (4) Stable operation of the cell was achieved for 100 hours at 300 oC and 140 cyclic currents operation at 600 oC. (5) Propane dissociation is the rate-limiting step among anodic step reactions. (6) The in-situ FT-IR results suggested that Ni-BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub>- heterogenous catalyst promotes the formation of CH<sub>4</sub>. The project successfully achieved the objectives and provided valuable insights into the electrode reaction mechanisms and rate-limiting steps through electrochemical characterizations and spectroscopy techniques.

研究分野：Materials Science and Engineering

キーワード：proton ceramic cells olefin production CO<sub>2</sub> reduction fuel cell catalysts membrane react or

科研費による研究は、研究者の自覚と責任において実施するものです。そのため、研究の実施や研究成果の公表等については、国の要請等に基づくものではなく、その研究成果に関する見解や責任は、研究者個人に帰属します。

様式 C-19、F-19-1、Z-19 (共通)

## 1. 研究開始当初の背景

Olefins such as propylene ( $C_3H_6$ ) and ethylene ( $C_2H_4$ ) are essential feedstocks for a vast array of chemical products, including plastics, fibers, packaging, and automotive parts. The demand for these olefins, particularly propylene, has increased dramatically in the past decades. Traditional propylene production is an energy-intensive process and requires precious catalysts (Pt, Re etc.) or toxic catalysts (CrOx, VOx etc.). Besides, massive energy is spent on separation or purification process.

Proton conducting solid oxide cells (P-SOC) that comprise of proton conductor and catalysts can realize efficient olefin production and  $CO_2$  recycling in use of external electricity (anodic reaction:  $C_3H_8 \rightarrow C_3H_6 + H_2$ , cathodic reaction:  $CO_2 + H_2 \rightarrow CO + CH_4 + H_2O$ ). It doesn't need separation process and is possible to exceed thermodynamic limitations with external electricity. However, they still face challenges including the high working temperature, low stability and low electrochemical performance.

## 2. 研究の目的

This project aimed to develop stable, efficient, and large-size P-SOCs for olefin production and  $CO_2$  reduction at low temperatures (eg. 400 °C). We also try to select suitable propane dehydrogenation reaction catalysts, propose rate-limiting steps, and understand reaction mechanisms by combining electrochemical methods and spectrum characterizations.

## 3. 研究の方法

### 3.1 Fabricate P-SOCs

Traditional cold-pressing fabrication method limits P-SOC size due to the uneven pressure and complex fabrication process. Here, we use tape-casting method to fabricate large-size planar P-SOCs and phase-inversion method to fabricate tubular P-SOCs. Fabrication processes including solvents, binders, pore former, and ceramic powders weight ratio were well-studied. We also optimized sintering temperatures to obtain P-SOCs with high electrochemical performance.

### 3.2 Catalyst selection and characterization

We cooperate with Prof. Shimizu research group from Hokkaido University, who is specialized in catalysts. They provided four catalysts with different functions (Table 1). We packed these catalysts on the top of P-SOC anode with same weight amount and evaluate P-SOC's electrochemical performance under  $C_3H_8$  fuels, then selecting the one with best performance for further tests. We also use GC and STEM to reveal their catalytic performance and morphology.

### 3.3 Electrochemical performance evaluation and exhaust gas analysis

We designed a new testing device to evaluate P-SOC electrochemical performance. The anode was injected with 20%  $C_3H_8$  while the cathode was injected with 30%  $H_2$ -10%  $CO_2$ /Ar. Online gas chromatography (GC) and mass spectroscopy (MS) were connected to P-SOC anode/cathode side exhaust gas. We analyzed gas composition change with temperatures

and applied currents.

### 3.4 Kinetic studies and FTIR analysis

Distribution relaxation of time (DRT) was used to investigate polarization resistance with the change of reaction gas compositions, then propose rate-limiting steps. We independently detected Ni, BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub>, Ni- BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> using in-situ FTIR, to analyze surface adsorbents under CO<sub>2</sub>-H<sub>2</sub> mixture gas, then proposing their respective functions during CO<sub>2</sub> reductions.

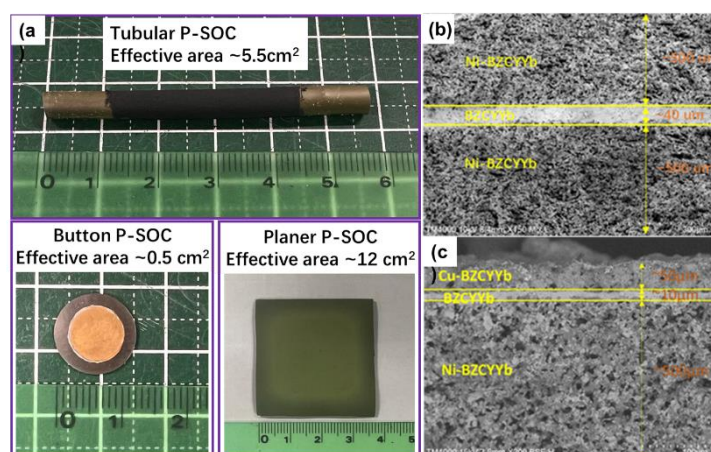
**Table 1** Catalysts and their specific function remarks

No.	sample	remarks
1	Pt0.5W03(25)/ZrO2	Great dehydrogenation reaction at 400 °C
2	Pt0.02/CeO2	Have surface proton conduction
3	Pt1/Nb2O5	Have electron conductivity
4	Pt5Mo7/TiO2	To prevent over dehydrogenation reaction, alloyed Pt

## 4. 研究成果

### 4.1 P-SOC configuration and electrochemical performance

Two cell configurations were prepared, they are: 1. Symmetrical cell configuration with Ni-BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> as anode and cathode, proton conductor BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> as electrolyte. This cell is designed to work from 300 °C to 400 °C, higher temperature leads to carbon deposition due to the nickel in the anode. 2. Cathode supported cell configuration with Cu- BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> as anode, Ni- BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> as cathode, and BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> as electrolyte. Due to the anti-carbon deposition property of copper, this cell could work from 400 °C to 600 °C. We also fabricated planer and tubular P-SOCs with different size (0.5cm<sup>2</sup> ~ 12cm<sup>2</sup>). As shown in Figure 1.

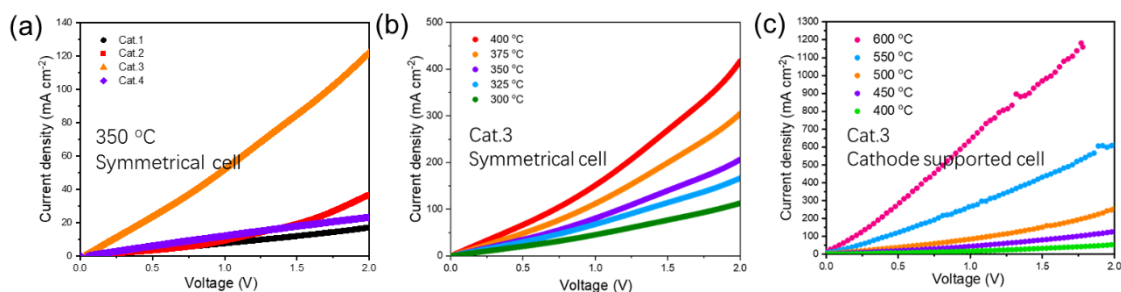


**Figure 1** (a) Optic photos of tubular P-SOC, button P-SOC, and planer P-SOC, they have different effective area size. SEM picture of (b) symmetrical cell, (c) cathode-

To compare catalysts catalytic performance towards propane dehydrogenation reaction, we packed catalysts No. 1-4 over symmetrical cell anode surface with a catalyst loading amount of 100 mg. The anode was fed to 50% C<sub>3</sub>H<sub>8</sub> while the cathode was fed to H<sub>2</sub>. Out of these four catalysts, catalyst 3 (Pt/Nb<sub>2</sub>O<sub>5</sub>) demonstrates best electrochemical

performance (Figure 2 (a)), indicating the electron conductivity has significant impact to the P-SOC's electrochemical performance, so we select catalyst 3 for further tests.

We further evaluated electrochemical performance of Pt/Nb<sub>2</sub>O<sub>5</sub>-loaded P-SOCs at different temperatures. Our results shown that in a symmetrical P-SOC configuration, the current density reached 416 mA cm<sup>-2</sup> at 400 °C and 112 mA cm<sup>-2</sup> at 300 °C with a 2V electrolysis voltage (Figure 2 (b)). To the best of our knowledge, this is the first time that P-SOC has been used at 300 °C to produce C<sub>3</sub>H<sub>6</sub> and reduce CO<sub>2</sub>, and our electrochemical performance was significantly higher than previously reported results for C<sub>2</sub>H<sub>6</sub> dehydrogenation reaction using P-SOC at 400 °C.<sup>1</sup> The high electrochemical performance demonstrate the unique advantage of the symmetrical cell configuration and great catalytic performance of Pt/Nb<sub>2</sub>O<sub>5</sub> catalyst. Furthermore, we were also able to produce olefin from 400 °C to 600 °C using a cathode-supported P-SOC, achieving a remarkable electrolysis current density of 1183 mA cm<sup>-2</sup> at 1.77 V at 600 °C (Figure 2 (c)). This high current density makes it feasible to detect outlet gas composition.



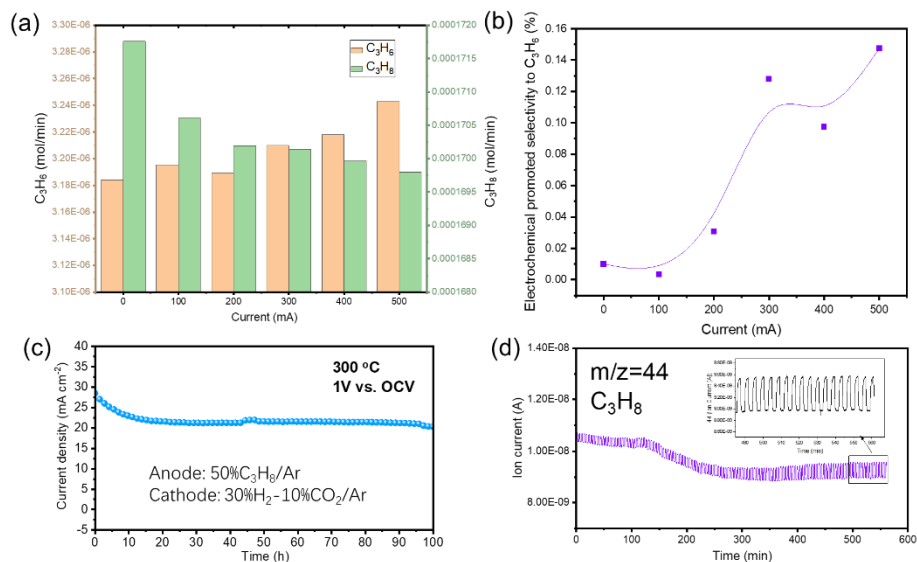
**Figure 2** I-V curves of (a) symmetrical P-SOC tested at 350 °C loaded with various catalysts. The anode was fed with 50%C<sub>3</sub>H<sub>8</sub>/Ar while the cathode was fed with H<sub>2</sub>. (b) Symmetrical P-SOC, and (c) cathode-supported P-SOC loaded with Pt/Nb<sub>2</sub>O<sub>5</sub> (Cat.3) catalyst working at various temperatures. The anode was fed with 20%C<sub>3</sub>H<sub>8</sub> while the cathode was fed with 30%H<sub>2</sub>-10% CO<sub>2</sub>/Ar.

## 4.2 Out-let gas compositions

GC results shown that C<sub>3</sub>H<sub>8</sub> can thermally decompose to C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, CO with the sum selectivity of 90.5%, among these products, olefins including C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> has the total selectivity up to 74.33%, proving major part of C<sub>3</sub>H<sub>8</sub> are thermodynamically converted to olefins. When applying external electricity, C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> are converted while C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> are generated, proving the external electricity promotes C<sub>3</sub>H<sub>8</sub> conversion (anodic reaction: C<sub>3</sub>H<sub>8</sub>→C<sub>3</sub>H<sub>6</sub>+H<sub>2</sub>, Figure 3 a). Importantly, the electrochemically promoted selectivity to C<sub>3</sub>H<sub>6</sub> increases with increasing currents, implying pumping H<sub>2</sub> to cathode side is prior to C<sub>3</sub>H<sub>8</sub> dehydrogenation reaction, the removal of hydrogen shifts propane dehydrogenation forward and thus enhancing propylene production (Figure 3 b). In cathode side, the cathodic CO<sub>2</sub> is also reduced by generated H<sub>2</sub> and form CO (cathodic reaction: H<sub>2</sub>+CO<sub>2</sub>→CO+ H<sub>2</sub>O).

## 4.3 Stability results of P-SOC

In this study, we did not observe severe carbon deposition in symmetrical P-SOCs when operating at temperatures below 400 °C, it operates stable for 100 hours at 300 °C (Figure 3 (c)). Additionally, when copper is used as the anode material in cathode-supported P-SOCs, cells were able to operate for 140 cycles (about 9 hours) at 600 °C with stable conversion of C<sub>3</sub>H<sub>8</sub> with applied currents, as shown in Figure 3 (d). These results demonstrate great stability of P-SOCs and show promising potential in the future applications.



**Figure 3** (a) Anodic C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> gas change with applied currents. (b) Electrochemical promoted selectivity to C<sub>3</sub>H<sub>6</sub> under various applied currents, the test temperature is 600 °C. (c) Stability results of symmetrical P-SOC works at 300 °C. (d) The propane signal change at 600 °C during cyclic current tests on cathode-supported P-SOC.

#### 4.4 Anodic rate-limiting step and cathodic reaction mechanisms

We use DRT method to interpret anodic elementary reactions in symmetrical P-SOCs. The results shown that when the anode was fed with 50% H<sub>2</sub>/Ar (P-SOC working as the hydrogen pump), the high-frequency resistances accounted for the most polarization resistance, indicating that proton migration or other high-frequency elementary processes is the rate-limiting step. However, when fed 50% C<sub>3</sub>H<sub>8</sub> to the anode, the middle-frequency resistance, which corresponds to surface processes such as dissociation and adsorption, should be the rate-limiting step. These findings suggest that developing catalysts with an enhanced propane dissociation ability could effectively improve the performance of the system.

FT-IR result indicates BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> is prone to adsorb CO<sub>2</sub> and form carbonates with different configurations, while nickel promotes the formation of CO. Interestingly, the Ni-BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> composites promote the formation of CH<sub>4</sub>. These findings suggest BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> working as a proton conducting channel and proton donor could facilitate methane formation.

#### Reference

- 1 Li, M. *et al. Nature Catalysis* **4**, 274–283 (2021).

5. 主な発表論文等

〔雑誌論文〕 計0件

〔学会発表〕 計1件（うち招待講演 0件 / うち国際学会 0件）

1. 発表者名 Nai Shi, Junji Hyodo, Ken-ichi Shimizu, Yoshihiro Yamazaki
2. 発表標題 Propylene production and CO2 recycling using proton conducting solid oxide cells (P-SOC)
3. 学会等名 Kyushu University Energy Week
4. 発表年 2023年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

-

6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
---------------------------	-----------------------	----

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
---------	---------