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1. Introduction

A direct methane-fueled proton-conducting ceramic fuel cell (PCFC) has been highlighted as an alternative energy technology to tackle the global energy and environmental challenges. Ceramic fuel cells generally operate at high temperature (>700 °C) and have been gaining attention for the past few years due to their high efficiency and impurity resistance.¹⁻⁴ While they are feasible for small- to large-scale applications, several technical issues should be resolved in order to commercialize these ceramic fuel cells. Particularly, they require high production costs and are susceptible to performance degradation due to their high operating temperature. This makes it crucially important to decrease the operating temperature of ceramic fuel cells.4-6 In terms of low temperature (350-550 °C) operation, PCFCs theoretically work better than solid oxide fuel cells (SOFCs) mainly because they rely on proton conduction which generally has a lower activation energy than oxygen ion conduction of SOFCs.^{5,7-12} In the meantime, to take advantage of ceramic fuel cells, PCFCs need to support internal hydrocarbon (e.g., CH₄) reforming in their anodes at such low temperatures. The internal steam reforming of methane can decrease the

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This study reports the catalytic performance of 8Ni (8 wt% Ni) and 6Ni2M (6 wt% Ni, 2 wt% M (M: Co, Cu, Rh)) anchored on $BaZr_{0.4}Ce_{0.4}Y_{0.1}Vb_{0.1}O_{3-\delta}$, an anode backbone material of proton-conducting ceramic fuel cells (PCFCs), for steam reforming of methane at low temperatures (350–550 °C). Results show that all catalysts have coherent structural properties and form bimetallic alloys. Their catalytic activities are evaluated at various temperatures, steam-to-carbon ratios, and gas flow rates. It is shown that 6Ni2Rh has the highest catalytic activity under all operating conditions. 6Ni2Rh and 6Ni2Co exhibit higher methane conversion and hydrogen yield than 8Ni even at low steam-to-carbon ratios. Their high activities make them less dependent on gas flow rate. They show higher resistance to carbon formation and maintain their catalytic activities during long-term operation. 6Ni2Rh and 6Ni2Co can respond to diverse operating conditions of direct methane-fueled PCFCs while maintaining high catalytic activity and stability.

overall cost by reducing the energy, system complexity, and costs required to obtain hydrogen from an external reformer installed outside a PCFC stack. PCFCs have been shown to tolerate carbon coking and impurity poisoning at intermediate temperatures (500-600 °C) with direct internal steam reforming of methane.13 However, the sluggish kinetics for internal steam reforming of methane and insufficient hydrogen supply at low temperature may prevent optimum power production. Given that steam reforming of methane is strongly endothermic (i.e., its heat of reaction is $\Delta H_{298K}^0 = +206 \text{ kJ mol}^{-1}$), lowering the temperature decreases its equilibrium constant and kinetic rates, which is highly important in determining fuel cell operating conditions, methane conversion, and hydrogen yield.¹⁴ Therefore, a novel catalyst is required in the PCFC anode to overcome such a barrier, ensuring the best performance at low temperature.

Addition of highly active catalysts to the existing anodes is crucial to facilitating an efficient internal steam reforming of methane in PCFCs at low temperature. Recently, the Ni-BZCYYb (BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3- δ}) anode has been extensively investigated to overcome the performance issues arising at low temperature while ensuring sufficient durability when being exposed to hydrocarbons.¹⁵ Ni supported by BZCYYb may function as an active catalyst for internal steam reforming of methane at 600 °C or higher.^{7,16,17} Thanks to its cost competitiveness, conventional metal catalysts for industrial steam reforming of methane are largely based on nickel as an active

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metal.¹⁸⁻²² Besides, nickel has a relatively high methane conversion efficiency and good H₂ selectivity at high temperature (>700 °C).23 However, despite many advantages of the Ni catalyst, its catalytic activity is substantially reduced at low temperature, and its use is restricted due to catalyst oxidation and carbon deposition.^{3,14,24,25} To overcome these problems, it is necessary to alloy Ni with a promoter metal that can enhance low-temperature reforming kinetics and resistance to carbon deposition. For example, many studies of hydrocarbon utilization have reported that the formation of a Ni-Co or Ni-Cu alloy reduces the carbon formation on the catalyst surface and improves catalytic performance.14,24,26,27 The Co contained in the Ni-Co alloy catalyst adsorbs O* and OH*, preventing carbon formation on its surface and improving catalytic activity.14,28 The Ni-Co alloy catalyst uses oxygen surface diffusion to oxidize the sulfur adsorbed on its surface, ensuring sulfur tolerance.29,30 On the other hand, the Cu contained in the Ni-Cu alloy catalyst highly accelerates the water gas shift reaction, producing more hydrogen, and suppresses coke deposition.14,24 It also has sulfur resistance because it weakens sulfur binding while reducing the adsorption energy of atomic sulfur.31 Bimetallic Ni-Rh catalysts have more carbon coking resistance and sulfur tolerance than the monometallic Ni catalyst.³²⁻³⁶ Moreover, alloying nickel with noble metals such as Rh has been proven to improve the catalytic activity and selectivity towards H2.14 The abovementioned metal promoters (i.e., Co, Cu, Rh) are applicable to internal steam reforming of methane in the PCFC anode at low temperature since these metals have the potential of oxygen affinity, carbon and sulfur resistance, and reforming of hydrocarbons and oxygenates.^{24,29-31,36-38} With commercialization in mind, although the cost efficiency from a material point of view may decrease by adding a promoter catalyst to pure Ni, Ni-based bimetallic alloys anchored on BZCYYb can be an effective option to guarantee sufficient internal steam reforming of methane at low temperature with substantial durability. In addition, the process of applying these additional catalysts to Ni the anode of PCFCs is simple without complex at manufacturing procedures using an infiltration method in which a solution of metal precursor is injected into the sintered anode.39-41 However, to date, there exist no attempts to study the effect of Ni-based bimetallic alloys anchored on BZCYYb on internal steam reforming of methane at low temperature.

This study aims to examine the catalytic activity and durability of Ni-based bimetallic alloys anchored on BZCYYb for internal steam reforming of methane at low temperature, and suggests a novel catalyst to overcome the aforementioned challenges. In this study, additional active metal catalysts such as Co, Cu, and Rh are introduced into Ni-BZCYYb, which forms Ni-based bimetallic alloys anchored on BZCYYb. Their microstructural and surface characteristics are examined by the Brunauer–Emmett–Teller method (BET), CO pulse chemisorption, X-ray diffraction (XRD), temperature programmed reduction (TPR), and transmission electron microscopy (TEM). Their catalytic activity and long-term stability for low-temperature steam reforming of methane are investigated by product gas analysis using gas chromatography, which elucidates the effect of the additional metal catalyst alloyed with Ni. The results obtained from this study suggest a candidate catalyst with high potential and feasibility as a PCFC anode material.

2. Experimental

2.1. Catalyst preparation

Monometallic Ni and Ni-based bimetallic catalysts were prepared by using the wet impregnation method and subsequent high-temperature reduction process. The powder of the support material BZCYYb (Kceracell, average size: 0.8 µm) was mixed with ethanol used as a solvent to avoid secondary phase formation. The volumetric ratio of the support to the solvent was 3 : 7. The dispersant (HypermerTM KD-6, Croda) was mixed with 3 wt% support to disperse it uniformly in the solvent mixture.42 Metal nitrates including Ni(NO₃)₂·6H₂O, Rh(NO₃)₃- $\cdot xH_2O$, Cu(NO₃)₂ $\cdot 3H_2O$, and Co(NO₃)₂ $\cdot 6H_2O$ (Sigma-Aldrich) were used to prepare metal precursors. The metal loading of all catalysts was fixed at 8 wt% with a Ni to M (i.e., Co, Cu, Rh) weight ratio of 3 to 1. These catalysts are named 8Ni (monometallic catalyst) and 6Ni2M (bimetallic catalyst). The metal precursor was mixed with BZCYYb in the solvent and stirred for 4 hours at room temperature. Then, the solvent was removed by drying at 100 °C overnight. Subsequently, the mixtures were calcined at 400 °C in air for 1 hour in a furnace. To make an alloy structure, the as-prepared (unreduced) catalysts were heated from room temperature to 700 °C with a heating ramp of 10 °C min⁻¹ while being reduced by using a mixed gas (10% H_2 in Ar (molar basis)) of 100 sccm and maintained for 2 hours under such environment.

2.2. Catalyst characterization

The structural properties and alloy formation of the 8Ni and 6Ni2M catalysts were examined by Brunauer-Emmett-Teller (BET), CO pulse chemisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and temperatureprogrammed reduction (TPR) methods. The BET analysis was conducted using a Quadrasorb SI (Quantachrome Instruments). Prior to the BET analysis, each catalyst sample was thermally pretreated in a vacuum for 15 hours at 250 °C to remove moisture and other contaminants adsorbed on the catalyst surface. Subsequently, the specific surface area of the pretreated samples was measured by N2 adsorption at 77 K. The XRD patterns of the catalysts were recorded by using a D8 Advance (Bruker) using Cu Ka radiation to obtain the crystal structure. The crystal structure of the catalysts was scanned with a step size of 0.02° s⁻¹ in the 2θ range = 25 to 80° . The TPR experiment was performed using 0.1 g of the unreduced catalyst sample placed in a U-tube reactor using an Autochem 2920 (Micromeritics) which includes a thermal conductivity detector (TCD). Inert gas He of 50 sccm was injected into the reactor at room temperature. Continuously, the sample was heated up to 200 °C for 1 hour and then cooled below 30 °C to obtain a clear solid surface of the catalysts. After pretreatment, the gas was changed to an active gas (10% H₂ in Ar (molar basis)) of 50 sccm, and then the temperature was raised up to 700 °C at a heating rate of 10 °C min⁻¹ while measuring hydrogen consumption

calculated by TCD. The CO pulse chemisorption experiment was carried out after the TPR experiment. After decreasing the sample temperature to 35 °C, He gas was used to purge the gas adsorbed on the sample surface. Subsequently, an active gas (10% CO in He (molar basis)) in the loop was supplied and pulsed repeatedly until adsorbed CO molecules saturated the catalyst surface. TEM analysis was performed to examine the structure and particle size of the catalysts, and energy dispersive X-ray spectrometry (EDS) was also conducted to obtain the information on chemical composition using a Talos F200X (FEI).

2.3. Catalyst activity test

The catalytic activity of the catalysts for steam reforming of methane was evaluated under various operating conditions including temperature, steam-to-carbon (S/C) ratio, and feed gas flow rate. The test was carried out by using a packed-bed quartz tube reactor ($D_{in} = 1.1$ cm) in a furnace containing a K-type thermocouple at atmospheric pressure, as shown in Fig. 1. To increase the accuracy of the experiment, 0.3 g of the unreduced catalyst was placed in the vicinity of the thermocouple inside the furnace. The height of catalysts in the reactor was nearly 0.21 cm with a catalyst volume of 0.2 cm³. The flow rate of gases including H₂, CH₄, and Ar was controlled using a mass flow controller (MKS Type 1179A). The partial pressure of steam in the humidifier was monitored using the saturation temperature to control the steam concentration in the feed gas. The composition of gas products exiting the reactor was measured by gas chromatography (Agilent 7890B) equipped with a dual TCD. The dual TCD was connected to two columns (HP-PLOT 5A: H₂, CO, and HP-PLOT-Q: CH₄, CO₂) which separate the mixed gases, respectively.

The methane conversion, $CH_{4,conv}$, and hydrogen yield, Y_{H2} , are calculated using the dry gas composition analyzed from gas chromatography and can be expressed using eqn (1) and (2),

respectively. The gas hourly space velocity, GHSV, can be expressed using eqn (3). Eqn (4) represents the degradation rate of active catalysts during a long-term stability test, which indicates the degree of carbon resistance.

$$CH_{4,conv} = \frac{Q_{CO} + Q_{CO_2}}{F_{CH_4}} \times 100$$
 (1)

$$Y_{\rm H_2} = \frac{Q_{\rm H_2}}{2F_{\rm CH_4} + F_{\rm H_2O}} \times 100 \tag{2}$$

$$GHSV = \frac{F_{\text{total}} \times 60}{\text{Vol}}$$
(3)

Degradation =
$$\frac{CH_{4,conv,0} - CH_{4,conv,t}}{CH_{4,conv,0}} \times 100$$
 (4)

where $CH_{4,conv}$: methane conversion [%]; Y_{H_3} : hydrogen yield [%]; GHSV: gas hourly space velocity $[h^{-1}]$; Degradation: the degree of methane conversion reduction compared to its initial value; Q_i : the volumetric flow rate of species *i* at the outlet [sccm]; F_i : the volumetric flow rate of species *i* at the inlet [sccm]; Vol: catalyst volume [cm³]; $CH_{4,conv,0}$: the methane conversion at the initial time; $CH_{4,conv,t}$: the methane conversion at time *t*. Given the methane conversion expressed by a reaction rate coefficient, *k*, in an Arrhenius form and the partial pressure of reactants, P_i ,

$$\begin{aligned} \ln(\mathrm{CH}_{4\mathrm{conv}}) &= \ln\left(\frac{k\left(P_{\mathrm{CH}_4}/P_{\mathrm{ref}}\right)^{\alpha}\left(P_{\mathrm{H}_2\mathrm{O}}/P_{\mathrm{ref}}\right)^{\beta}}{F_{\mathrm{CH}_4}}\right) \\ &= \ln\left(\frac{\left(P_{\mathrm{CH}_4}/P_{\mathrm{ref}}\right)^{\alpha}}{X_{\mathrm{CH}_4}}\right) - \left(\frac{E_{\mathrm{a}}}{R}\right)\frac{1}{T} + \beta\,\ln\left(P_{\mathrm{H}_2\mathrm{O}}/P_{\mathrm{ref}}\right) \\ &+ \ln\left(\frac{A \times 60}{\mathrm{Vol} \times \mathrm{GHSV}}\right) \end{aligned}$$

where *A*: pre-exponential factor [sccm]; E_a : activation energy [kJ mol⁻¹]; *R*: universal gas constant [J mol⁻¹ K⁻¹]; *T*: temperature



Fig. 1 Schematic diagram of the catalytic activity test facility equipped with online gas chromatography.

Table 1 Catalytic activity and long-term stability test conditions

Test type	Temperature [°C]	Steam-to- carbon ratio	Gas flow rate [sccm] $(GHSV [h^{-1}])$
Temperature Steam-to-	350–550 500	S/C = 2 S/C = 2, 1, 0.5	100 (30 000) 100 (30 000)
Gas flow rate	500	S/C = 1	150 (45 000), 100 (30 000) 50 (15 000)
Stability	500	S/C = 0.1	50 (15 000)

[K]; X_{CH4} : mole fraction of methane in the feed gas; α : the order of reaction with respect to P_{CH4} ; β : the order of reaction with respect to P_{H2O} . Note that the first term on the right hand side is maintained constant throughout the catalytic activity test. The effect of the second, third, and fourth term on the right hand side will be elucidated in Section 3.2.1, 3.2.2, and 3.2.3, respectively.

The effects of temperature, S/C ratio, and feed gas flow rate on the catalytic activity were investigated, followed by a longterm stability test. Prior to the test, the catalyst samples were subjected to a high-temperature reduction process forming an in situ alloy. The operating conditions for the activity test and long-term stability test conditions considered in this study are summarized in Table 1. The carbon formation regime in equilibrium under these operating conditions was confirmed from the ternary diagram shown in Fig. S1.[†] In equilibrium, the S/C ratio of 2 makes the reaction environment free of carbon formation (Fig. $S2(a)^{\dagger}$), but it falls in the carbon formation regime at the S/C ratio less than 1 at 500 °C (Fig. S2(b)†). The equilibrium values under given operating conditions were calculated by using the software NASA CEA (at T, P = constant). Throughout the catalytic activity test, the molar fraction of methane and operating pressure were maintained constant at 20% and 1 atm, respectively. The effect of temperature was elucidated by changing the temperature from 350 °C to 550 °C with a feed gas flow rate of 100 sccm and an S/C ratio of 2. The effect of the S/C ratio was examined by changing it from 2 to 0.5 while maintaining the gas flow rate and temperature constant at 100 sccm and 500 °C, respectively. The effect of the feed gas flow rate was investigated by changing it from 150 sccm to 50 sccm

Table 2 Structural properties (*i.e.*, specific surface area, metallic particle diameter, metallic surface area, and metal dispersion) of 8Ni and 6Ni2M catalysts

Sample	Specific surface area ^{<i>a</i>} [m ² g ⁻¹]	Metallic particle diameter ^b [nm]	Metallic surface area ^b $[m^2_{M}/g_{cat}]$	Metal dispersion ^b [%]
BZCYYb	27	_	_	_
8Ni	9	27	2.0	3.8
6Ni2Co	8	32	1.7	3.1
6Ni2Cu	9	38	1.4	2.7
6Ni2Rh	9	23	2.2	4.5

^a BET. ^b CO pulse chemisorption.

while maintaining the temperature and S/C ratio constant at 500 $^{\circ}$ C and 1, respectively. The long-term stability was evaluated by using harsh conditions (temperature: 500 $^{\circ}$ C, gas composition: methane with 9.1% steam, gas flow rate: 50 sccm) which induce carbon formation.

3. Results and discussion

3.1. Catalyst characterization

The coherent structural properties of the 8Ni and 6Ni2M catalysts, as summarized in Table 2, imply the reliability of the synthesis method and provide the same basis for catalytic performance evaluation. The specific surface area of the catalysts was examined by BET analysis. The bare support BZCYYb has a specific surface area of 27 m² g⁻¹, while the 8Ni and 6Ni2M catalysts have specific surface areas of 8–9 m^2 g^{-1} . The lower specific surface area of the catalysts is attributed to the high metal loading amount (8 wt%) and the pore blockage by impregnation.²⁰ If larger catalyst particles are deposited on the support, it may induce substantial pore blockage and lower gas diffusion rates, particularly at the anode of a full cell. Nevertheless, given that the specific surface areas of these catalysts show little deviation, it can be argued that their catalytic activities can be compared on the same basis of surface sites. This argument is further strengthened by the surface information of the catalysts for the metal formed on the support, obtained through CO pulse chemisorption experiments. As evidenced in Table 2, the metallic particle diameter and the metallic surface area are in the range of 23–38 nm and 1.4–2.2 m_M^2/g_{cat} , respectively, for these catalysts. The metal dispersion is in the range of 2.7-4.5%. All these metallic structural indices show similar values with respect to various metal species impregnated on the support, which indicates the reproducibility and reliability of catalyst synthesis. Along with the consistent specific surface area, these metallic structural properties with small deviation provide the same ground on which catalytic activities can be investigated.

In addition to the coherent structural properties, all bimetallic catalysts form an alloyed state between Ni and promoter M (M: Co, Cu, Rh) metal. Given that the performance of the Nibased bimetallic catalysts relies heavily on the formation of an alloyed state between Ni and promoter M metal, XRD analysis is crucial to determining whether the alloy is properly formed during the fabrication process. Fig. 2 shows the overall XRD patterns of the bare support BZCYYb, 8Ni and 6Ni2M catalysts. There is no peak in BZCYYb between 43 and 45°, whereas the catalysts have a metal peak in this peak range, which is highlighted and magnified using a red dotted box in Fig. 2. It can be evidenced that the XRD peaks of the 6Ni2M catalysts are located at a lower degree than those of the 8Ni catalyst. To elucidate this further, the monometallic (8M) catalysts were fabricated in the same manner described above and were characterized under the same conditions to compare with the 8Ni and 6Ni2M catalysts (refer to Fig. S3[†]). Each of the metal peaks observed in Fig. 2 is compared with the monometallic (8M) peak, as can be seen in Fig. S3.† It can be evidenced that the metal peak in the bimetallic (6Ni2M) catalysts



Fig. 2 X-ray diffraction patterns of BZCYYb (—), 8Ni (—), and 6Ni2M (M: — Co, — Cu, — Rh) catalysts. Support peak: BZCYYb(4411); metal peaks: • Ni, • Ni–Co alloy, • Ni–Cu alloy, • Ni–Rh alloy.

shifts towards the middle of the two metal peaks observed in the corresponding monometallic (8Ni and 8M) catalysts, which confirms the successful alloy formation. Specifically, as shown in Fig. S3(a),† the alloyed metal peak of 6Ni2Co appears at 44.6° in between the 8Ni metal peak at 44.7° (Ni(111), PDF 04-001-3156) and 8Co metal peak at 44.4° (Co(111), PDF 04-006-8067).⁴³⁻⁴⁵ Likewise, the alloy peak of 6Ni2Cu is located at 44.4° which is between 8Ni (44.7°) and 8Cu (43.4°, Cu(111), PDF 04-003-5318) metal peaks, as shown in Fig. S3(b).† ^{46,47} In the same way, Fig. S3(c)† shows that the alloy peak of 6Ni2Rh exists at 44.3° between that of 8Ni (44.7°) and that of 8Rh (41.2°, Rh(111), PDF 04-016-1279).⁴⁸ Therefore, considering the peak location of the alloyed metal catalysts, it can be discussed that all bimetallic (6Ni2M) catalysts formed alloys, which is further demonstrated by TEM analysis as follows.

The structure analysis of all catalysts by TEM confirms again their alloy formation and demonstrates nano-sphere particles anchored on the BZCYYb support. EDS mapping was performed to analyze the chemical composition of the metal distribution and alloy structure. As shown in Fig. 3, the 8Ni and 6Ni2M catalysts are in the form of nano-sphere particles of size less than about 30 nm. In addition, EDS mapping analysis confirms that the metal particles are anchored on BZCYYb consisting of large and heavy atoms (Ba, Zr, Ce, Y, Yb, O). Moreover, nickel and promoter metals (M: Co, Cu, Rh) are found to be located at the same location, which clarifies the fact that two different metals were successfully alloyed. Fig. S4[†] provides extra information which helps to check the size and uniformity of the metal particles in more detail. In Fig. S4(a),† the Ni particles of the 8Ni catalyst are generally 10-30 nm in size and are evenly spread on the support. As shown in Fig. S4(b),† 6Ni2Co has a metal particle size and distribution similar to 8Ni. In addition, the positions of Ni and Co are the same and they are arranged on the support elements. Thus, it can be inferred that the

6Ni2Co catalyst is an alloy and is well supported on BZCYYb. In the case of the 6Ni2Cu catalyst, Fig. S4(c)† shows the same trend as that for the 6Ni2Co catalyst. As shown in Fig. S4(d),† the 6Ni2Rh catalyst has the same tendency of uniformity as that of other bimetallic catalysts (6Ni2Co and 6Ni2Cu). The size of the alloyed metal particles is smaller (less than about 20 nm) than that of other catalysts. Overall, the metal particle sizes of the catalysts obtained from the TEM images are similar to the metallic particle diameter provided in Table 2.

The alloy formation enhances the reducibility of the 6Ni2M catalysts compared to that of the 8Ni catalyst. Fig. 4 shows the results of TPR experiments that examine the reducibility of the 8Ni and 6Ni2M catalysts. The 8Ni catalyst has a reduction temperature range of 220-340 °C in which Ni shows a peak at 338 °C, which is associated with the reduction of relatively free NiO particles. The broad peak at higher temperature (340-500 °C) results from a strong interaction of Ni with the support.^{20,49} The support (BZCYYb) located at the bottom shows no reduction. When a bimetallic catalyst is formed, the degree of reduction changes due to the interaction between alloyed metals.44,50 It can be observed that the reduction temperature of the 6Ni2M catalysts is located at a lower temperature than that of the 8Ni catalyst. In addition, since the 6Ni2M catalysts formed an alloy as verified by the results of XRD, they show one stage reduction like the reduction profile of 8Ni.27,51 To elucidate further the effect of alloy formation on the reducibility, the monometallic (8M) catalysts were characterized under the same conditions to compare with the 8Ni and 6Ni2M catalysts, as shown in Fig. S5.† It can be seen that the reducibility of the 6Ni2M catalysts is improved compared to that of the 8Ni catalyst, attributed to the alloyed structure of the 6Ni2M catalysts. In the reduction profile of 8Co in Fig. S5(a),† the first peak (249 °C) is the reduction step from Co₃O₄ to CoO, and the second peak (318 °C) is the reduction step from CoO to Co.52 In the case of



Fig. 3 TEM and EDS mapping images of (a) 8Ni; (b) 6Ni2Co; (c) 6Ni2Cu; (d) 6Ni2Rh.

6Ni2Co, since Ni and Co are alloyed with each other, the temperature of the reduction peak is at 325 °C which is between that of 8Ni and 8Co.^{44,50} In Fig. S5(b),† 8Cu has two reduction peaks at 257 °C and 299 °C. The peak at lower temperature is the reduction of the copper oxide cluster, and the other peak at higher temperature is associated with bulk copper.^{47,53-55} Affected by the interaction of both Ni and Cu, the reduction peak of 6Ni2Cu is located at 332 °C.⁴⁶ Fig. S5(c)† shows that the Rh in the 6Ni2Rh catalyst significantly improves the reducibility of Ni through the synergy effect of the alloy.^{56,57} The peak at 139 °C in the 8Rh reduction profile represents the reducion of Rh₂O₃. The peak of 6Ni2Rh at 240 °C is due to the interplay of Rh and Ni.

3.2. Catalytic activity test

Based on the confirmed alloy structure with coherent nanoscale particles, the catalytic activities of 6Ni2M for steam reforming of methane at low temperature were evaluated. To be applicable in the anode of PCFCs, catalysts should have high activity and high hydrogen yield so that they can supply sufficient hydrogen reformed internally from methane and steam. In this regard, experiments were performed under conditions of various operating temperatures (350–550 °C), steam-to-carbon ratios (0.5–2), and gas flow rates (50–150 sccm), all of which are feasible operating conditions for PCFC unit-cells.

3.2.1. Effect of temperature. The 6Ni2Rh catalyst shows superior activity with substantial hydrogen yield at all temperatures compared to 8Ni and other 6Ni2M catalysts, attributed to its low activation energy for the overall reaction. The first activity test was carried out to elucidate the effect of temperature (350-550 °C) at a flow rate of 100 sccm and an S/C ratio of 2, which falls in a carbon-free field at equilibrium. As shown in Fig. 5(a), the order of methane conversion and hydrogen yield is 6Ni2Rh > 8Ni > 6Ni2Co > 6Ni2Cu in all temperature regions. All



g. 4 Temperature-programmed reduction profiles of BZCYYb (—), 8Ni (—) and 6Ni2M (M: — Co, — Cu, — Rh) catalysts.

catalysts tend to decrease methane conversion and hydrogen yield as the temperature is lowered, during which the reduction rate of 6Ni2Rh is substantially smaller than that of other catalysts. Particularly, 6Ni2Rh exhibits catalytic activity even below 400 °C where 8Ni and other 6Ni2M catalysts are inactive. It maintains not only methane conversion, but also hydrogen yield which is critical for PCFC operation. This implies that PCFCs may potentially expand their operating regime below 400 °C, with the aid of the Ni-Rh bimetallic alloy catalyst fabricated in their anode. Such a dependence on temperature is further explained by their activation energy, as shown in Fig. 5(b). It can be observed that the order of activation energy is opposite to that of methane conversion: $6Ni2Rh (39.3 \text{ kJ mol}^{-1})$ < 8Ni $(E_a(1) = 68.6 \text{ kJ mol}^{-1}, E_a(2) = 150.5 \text{ kJ mol}^{-1}) < 6\text{Ni}2\text{Co}$ $(E_a(1) = 92.9 \text{ kJ mol}^{-1}, E_a(2) = 160.1 \text{ kJ mol}^{-1}) < 6\text{Ni}2\text{Cu}(E_a(1) = 160.1 \text{ kJ mol}^{-1})$ 110.5 kJ mol⁻¹, $E_a(2) = 174.8$ kJ mol⁻¹). The activation energy of 6Ni2Rh is 1.7-4.4 times less than that of 8Ni and other 6Ni2M catalysts. In particular, its activation energy is consistently low throughout the temperature, while that of other catalysts increases substantially below 500 °C (*i.e.*, $E_a(1)$ to $E_a(2)$ shown in Fig. 5(b)). The low activation energy of 6Ni2Rh supports its catalytic activity, especially in the low temperature regime. Note that the calculated activation energy for the dissociation of methane (i.e., rate-limiting step) on the (111) Ni surface, reported by Nikolla *et al.*,⁵⁸ is in the range of 70–125 kJ mol⁻¹, into which the activation energy of 8Ni falls. It can be inferred that the Ni-Rh bimetallic alloy formation contributes to lowering the activation energy of the rate-limiting step of the Ni monometallic catalyst, promoting methane conversion and hydrogen yield in the low temperature regime.

The 6Ni2Co and 6Ni2Cu catalysts exhibit comparable or lower catalytic activity in comparison with the 8Ni catalyst due to their high activation energy for the onset of steam reforming. The methane conversion and hydrogen yield of 6Ni2Co and 6Ni2Cu are lower than those of 8Ni, as shown in Fig. 5(a), due to their high activation energy evidenced in Fig. 5(b). In the case of 6Ni2Co, O^{*} and OH^{*} produced from H₂O could be strongly

adsorbed to cobalt contained in 6Ni2Co at this S/C ratio, which makes the surface of 6Ni2Co poisoned by O*, as reported by Jones et al.28 It can be inferred that O* poisoning on the 6Ni2Co surface hinders the dissociative adsorption of methane on its surface compared to the 8Ni catalyst. Therefore, the methane conversion and hydrogen yield of 6Ni2Co could be lower than those of 8Ni under steam rich conditions, which is further elucidated in the following section. In the case of 6Ni2Cu, the methane conversion and hydrogen yield are significantly lower than those of other catalysts due to its highest activation energy. Bian et al. reported that methane is adsorbed predominantly on the copper surface since the copper contained in 6Ni2Cu has not only lower surface energy than nickel, but also slow kinetics of methane dissociation, which suppresses the methane activation.37 An et al. also reported that the activation energy for methane dissociation on the (111)Cu/Ni surface is about 1.3 times larger than that on the (111)Ni surface.⁵⁹ In this study, the activation energy of 6Ni2Cu is also approximately 1.3 times larger than that of 8Ni, from which it can be inferred that Ni-Cu alloy formation reduces the methane dissociation rate and hence methane activation.

Based on the results, it can be discussed that further catalytic activity testing should be needed at other S/C ratios (*i.e.*, partial pressure of steam) at low temperature. The operating temperature of 500 °C seems appropriate for the following study given that relatively sufficient or measurable catalytic activities are observed at around 500 °C below which the activation energies of 8Ni, 6Ni2Co, and 6Ni2Cu increase. Indeed, a number of previous studies related to low temperature SOFCs and PCFCs^{5,8,13,15,60} have been performed at 500 °C with various S/C ratios, as follows.

3.2.2. Effect of steam-to-carbon ratio. The second activity test was performed to verify the catalytic activity of 6Ni2M catalysts at different S/C ratios (*i.e.*, 2, 1, 0.5). From the perspective of PCFC system integration, a low S/C ratio is preferable due to low thermal energy requirement for steam supply,





Fig. 5 Effect of temperature on steam reforming of methane by 8Ni and 6Ni2M catalysts under carbon-formation-free conditions. (a) CH₄ conversion (--- equilibrium, ■ 8Ni, ■ 6Ni2Co, ■ 6Ni2Cu, ■ 6Ni2Rh) and hydrogen yield (○ 8Ni, ○ 6Ni2Co, ○ 6Ni2Cu, ○ 6Ni2Rh); (b) activation energy (■ 8Ni, ▲ 6Ni2Co, ▼ 6Ni2Cu, ◆ 6Ni2Rh). Variable: temperature = 350-550 °C. Fixed conditions: pressure = 1 atm, S/C ratio = 2 (CH₄: 20%, H₂O: 40%, Ar: 40% (H₂O/CH₄ = 2)), gas flow rate = 100 sccm.

resulting in a high energy conversion efficiency.³² In addition, the support BZCYYb may undergo phase change when being exposed to high partial pressure of steam, making it necessary to reduce the steam concentration in its anode.⁴² In this regard, the activity test was conducted by decreasing the S/C ratio to elucidate its effect on the catalytic performance. The other operating conditions including a temperature of 500 °C and a gas flow rate of 100 sccm were maintained constant. Note that eqn (2) implies that the hydrogen yield varies with the hydrogen production rate, which is dependent on methane conversion, and the amount of hydrogen-containing reactants (*i.e.*, CH₄ and H₂O), dictated by the S/C ratio. Their relative variation is examined in the following.

The 6Ni2Rh catalyst maintains a high methane conversion and hydrogen yield at all S/C ratios, in particular at a high steam

Fig. 6 Effect of steam-to-carbon ratio on steam reforming of methane by 8Ni and 6Ni2M catalysts. (a) CH₄ conversion (--- equilibrium, ■ CH₄: 20%, H₂O: 40%, Ar: 40% (H₂O/CH₄ = 2); ■ CH₄: 20%, H₂O: 20%, Ar: 60% (H₂O/CH₄ = 1); ■ CH₄: 20%, H₂O: 10%, Ar: 70% (H₂O/CH₄ = 0.5)) and hydrogen yield (•); (b) the order of reaction with respect to P_{H₂O} (■ 8Ni, ▲ 6Ni2Co, ▼ 6Ni2Cu, ◆ 6Ni2Rh). Variable: S/C ratio = 2, 1, 0.5. Fixed conditions: pressure = 1 atm, temperature = 500 °C, gas flow rate = 100 sccm.

concentration given its resistance to oxide formation. Fig. 6(a) shows that methane conversion and hydrogen yield of 6Ni2Rh are higher than those of 8Ni, as the S/C ratio is raised. Particularly, 6Ni2Rh's activity is much stronger than that of 8Ni at the S/C ratio of 2. The change in 6Ni2Rh's methane conversion and hydrogen yield is more evident when the S/C ratio is raised from 1 to 2. This is further evidenced by its order of reaction with respect to P_{H_2O} , as shown in Fig. 6(b). It can be observed that 6Ni2Rh has a $\beta(2)$ higher than $\beta(1)$, whereas those of 8Ni change in the opposite way. The high activity of 6Ni2Rh provides a reaction rate as high as the increase of reactants, which results in a high hydrogen yield and β along with an increase of the S/C ratio. On the other hand, the increase of 8Ni's reaction rate does not match the increase of S/C ratio, in particular from 1 to 2, making the hydrogen yield and β to decrease above the S/C ratio

of 1. It can be inferred that such a high partial pressure of steam forms an oxidizing environment, where the oxidation of 8Ni occurs and lowers the activity.^{61–63} However, the rhodium contained in 6Ni2Rh has the ability of hydrogen spill-over, which inhibits the formation of metal-oxide and maintains its metallic form even at a high S/C ratio.⁶⁴ This feature corresponds to the reducibility of 6Ni2Rh and 8Ni, as observed in Fig. 4. 6Ni2Rh has a higher reducibility than 8Ni, providing oxidation resistance and maintaining the metallic form in its surface.

The 6Ni2Co catalyst shows higher catalytic activity than 8Ni, as the S/C ratio is lowered, indicating its feasibility as a reforming catalyst in the anode of PCFCs. Fig. 6(a) shows that the methane conversion and hydrogen yield of 6Ni2Co peak at the S/C ratio of 1 and maintain a higher value than those of 8Ni, as the S/C ratio is further lowered to 0.5. As evidenced in Fig. 6(b), 6Ni2Co's order of reaction with respect to P_{H_2O} changes the sign of its slope (from the negative to the positive) at around the S/C ratio of 1 and becomes larger than that of 8Ni, when the S/C ratio is lowered from 2 to 1. This is explained by its high oxygen affinity and resistance to methane adsorption at high partial pressure of steam (e.g., the S/C ratio of 2),^{28,65} as explained in Section 3.2.1. In contrast, at the S/C ratios of 1 and 0.5, the catalytic activity of 6Ni2Co is enhanced significantly due to overcoming the surface poisoning by O* and resistance to methane adsorption. 6Ni2Co's ability to reform methane and produce hydrogen becomes evident at low partial pressure of steam.66 Its methane conversion and hydrogen yield at the S/C ratios of 1 and 0.5 are comparable to those of 6Ni2Rh, confirming their high catalytic activity at low partial pressure of steam. Note that the high hydrogen yield of 6Ni2Co at the low S/ C ratio is particularly desirable for PCFC application. Its product selectivity towards hydrogen makes it a promising catalyst for the PCFC anode where sufficient hydrogen, as well as internal methane reforming rate, is required. On the other hand, 6Ni2Cu shows lower methane conversion and hydrogen yield than 8Ni under all conditions, making its application to the PCFC anode difficult.

Lowering the S/C ratio, desirable for PCFC operation, reveals that both 6Ni2Rh and 6Ni2Co are promising catalysts for internal reforming of methane in the PCFC anode. In particular, they provide substantial methane conversion and hydrogen yield at the S/C ratio of 1 (and at a temperature of 500 °C). Considering the relative cost of Co and Rh, the catalytic activity of the former makes it attractive as a candidate material when alloyed with Ni in the PCFC anode for direct hydrocarbon feed. To verify further their catalytic activity and feasibility for PCFCs, the effect of gas flow rate is elucidated at the S/C ratio of 1 and temperature of 500 °C as follows.

3.2.3. Effect of gas flow rate. The third catalytic activity test was conducted by changing the feed gas flow rate. During PCFC operation, the anode gas flow rate determines fuel utilization (defined as the ratio of fuel consumed to fuel supplied) along with electrical current imposed on PCFC unit-cells. Controlling the fuel utilization upon the variation of electrical demand is critical in maintaining the electrochemical environment in the anode, making it necessary to change accordingly the anode gas flow rate. In this regard, all catalysts were evaluated at various

gas flow rates (*i.e.*, 150, 100, 50 sccm) to examine the effect of the feed gas flow rate on their catalytic activity. Other conditions including the temperature and the S/C ratio were maintained constant at 500 $^{\circ}$ C and 1, respectively.

The methane conversion and hydrogen yield of 6Ni2Rh are maintained at high values even at a large gas flow rate, and those of 6Ni2Co approach 6Ni2Rh's activity, as the gas flow rate is lowered. Fig. 7(a) shows that the methane conversion and hydrogen yield of all catalysts increase with a decrease of the gas flow rate, during which the order of catalytic activities is 6Ni2Rh > 6Ni2Co > 8Ni > 6Ni2Cu. As indicated by eqn (1) and (2), lowering the feed gas flow rate increases the methane conversion and hydrogen yield for a given reaction rate.²⁰ On the other hand, their response to changes in the gas flow rate varies from catalyst to catalyst, attributed to different catalytic activities or reaction rates. The high catalytic activity of 6Ni2Rh, evidenced



Fig. 7 Effect of gas flow rate on steam reforming of methane by 8Ni and 6Ni2M catalysts. (a) CH₄ conversion (--- equilibrium, ■ 150 sccm, ■ 100 sccm, ■ 50 sccm) and hydrogen yield (•); (b) the dependence on the gas hourly space velocity, represented by its slope or time scale needed for methane conversion (■ 8Ni, ▲ 6Ni2Co, ▼ 6Ni2Cu, ◆ 6Ni2Rh). Variable: gas flow rate = 150, 100, 50 sccm. Fixed conditions: pressure = 1 atm, temperature = 500 °C, S/C ratio = 1 (CH₄: 20%, H₂O: 20%, Ar: 60% (H₂O/CH₄ = 1)).

so far, results in a large reaction rate for steam reforming of methane and hence high methane conversion and hydrogen yield at all gas flow rates. This makes 6Ni2Rh less dependent on the variation of the gas flow rate, confirming its feasibility as the PCFC anode catalyst under diverse operating conditions. In the meantime, 6Ni2Co provides a reaction rate as high as that of 6Ni2Rh, when the gas flow rate decreases to 50 sccm, as shown in Fig. 7(a). It can be inferred that, with a sufficient residence time (*i.e.*, low gas flow rate), 6Ni2Co's catalytic activity is as strong as that of 6Ni2Rh, improving its applicability to the PCFC anode. Note that the high fuel utilization is desirable for enhancing the energy conversion efficiency of a PCFC system, for which the feed gas flow rate needs to be reduced. In this sense, 6Ni2Co can be a promising catalyst, as good as 6Ni2Rh, for the PCFC anode.

The high catalytic activity of 6Ni2Rh and 6Ni2Co makes them less dependent on the gas hourly space velocity. Fig. 7(b) shows the dependence of catalysts on the gas hourly space velocity, in which the slope represents the time scale required for methane conversion. The higher the time scale or the slope, the lower the catalytic activity. It can be observed that 6Ni2Rh has the smallest time scales $(t(1) = 1.19 \times 10^{-2} \text{ s}, t(2) = 1.02 \times 10^{-2} \text{ s})$, indicating its high catalytic activity and low dependency on the gas hourly space velocity. 6Ni2Co also has small time scales $(t(1) = 3.61 \times 10^{-2} \text{ s},$ $t(2) = 4.89 \times 10^{-2}$ s), which makes it less dependent on the gas hourly space velocity, in particular at the low gas flow rate region (*i.e.*, region (1)). This corresponds to the results shown in Fig. 7(a). The high catalytic activity of 6Ni2Rh and 6Ni2Co results in a short time needed for converting methane through steam reforming reactions. Based on such small time scales, the gas hourly space velocity, which dictates the residence time, has a limited effect on their methane conversion. This feature is substantially important when accounting for diverse anode gas flow rates and providing sufficient internal methane reforming and hydrogen production in the PCFC anode. In contrast, the time scales for 8Ni ($t(1) = 8.87 \times$ 10^{-2} s, $t(2) = 9.48 \times 10^{-2}$ s) and 6Ni2Cu ($t(1) = 7.56 \times 10^{-2}$ s, t(2) $= 6.92 \times 10^{-2}$ s) are higher than those of 6Ni2Rh and 6Ni2Co at all gas hourly space velocities, which implies their low catalytic activities.

Based on the results shown above, 6Ni2Rh and 6Ni2Co are promising candidates for the PCFC anode catalyst. The former maintains the high methane conversion and hydrogen yield under various operating conditions including temperature, S/C ratio, and feed gas flow rate. In the meantime, the latter shows comparable catalytic activity at low S/C ratio and low feed gas flow rate which are desirable operating conditions for enhancing the efficiency of a PCFC system. Given their catalytic activity and feasibility as the PCFC anode material, their stability needs to be demonstrated, which is discussed in the following.

Carbon resistance and stability

The 6Ni2Rh and 6Ni2Co catalysts show higher resistance to carbon formation and stability than 8Ni, confirming again their feasibility as the PCFC anode material. The stability test was conducted to elucidate the resistance to carbon deposition of

8Ni, 6Ni2Co, and 6Ni2Rh at a very low S/C ratio of 0.1, where carbon deposition occurs predominantly from a thermodynamic point of view. Such harsh conditions were considered to accelerate their degradation and investigate their stability within a short period of time. As shown in Fig. 8, although all catalysts exhibit decreasing methane conversion rates with operating time, there are obvious discrepancies between catalysts. 6Ni2Rh and 6Ni2Co show lower degradation rates of 3.3% and 10.5%, respectively, than Ni (24.8%), during the 30 h operations. The activity degradation of 6Ni2Co and 8Ni is substantial in the beginning of the experiment, while the degradation of 6Ni2Co reduces to a small value with time. In contrast, the degradation of 8Ni proceeds continuously throughout the operating time. Generally, nickel is known to be susceptible to carbon deposition, but in this experiment, 8Ni exhibits a relatively long active methane conversion period. This phenomenon can be explicated by the PCFC anode support material BZCYYb which has robust carbon resistance.13 Furthermore, OH* which is generated by hydrolysis is spilled over, thereby removing carbon deposited over the Ni surface.⁵ On top of such a support effect, in comparison with the monometallic Ni catalyst, the Ni-Rh alloy has higher activation energy of the C-C bond, which prevents carbon deposition on the catalyst surface, and lower C-O formation activation energy, which helps to remove carbon deposited on the catalyst surface, elucidated by computational analysis.32 Indeed, 6Ni2Rh shows less carbon deposition than 8Ni, as shown in Fig. S6.† Moreover, the catalyst particles of 6Ni2Rh were not separated from the BZCYYb, whereas those of 8Ni were detached from the support along with the growth of carbon nanofibers. This feature further enhances 6Ni2Rh's resistance to carbon formation on its surface, which explains its lower degradation rate



Fig. 8 Change in methane conversion during steam reforming of methane by 8Ni, 6Ni2Rh, and 6Ni2Co catalysts under high carbon formation conditions. CH₄ conversion (\square 8Ni, \triangle 6Ni2Co, \diamondsuit 6Ni2Rh). Fixed conditions: pressure = 1 atm, temperature = 500 °C, S/C ratio = 0.1 (CH₄: 90.9%, H₂O: 9.1% (H₂O/CH₄ = 0.1)), gas flow rate = 50 sccm.

than 8Ni. In the case of 6Ni2Co, the high oxygen affinity of the Ni-Co alloy, discussed above, may enable O* and OH* adsorbed on its surface to enhance the oxidation of carbon, thereby restraining carbon deposition. Similar to the results of 6Ni2Rh, Fig. S6[†] shows that the carbon deposition on the 6Ni2Co surface is less than that on 8Ni. The surface effect of 6Ni2Rh and 6Ni2Co improves their carbon resistance and long-term stability, which enhances their feasibility as the direct hydrocarbon-fueled PCFC anode material. Given that a recent study demonstrated the feasibility of PCFCs based on internal dry reforming of methane,67 the enhanced carbon resistance and long-term stability of 6Ni2Rh and 6Ni2Co can extend the operating regime of PCFCs from steam reforming to dry reforming. However, long-term tests over 100 to 1000 hours may result in surface diffusion and Ostwald ripening of nano-scale catalyst particles, which induces particle growth and activity degradation. This will be further examined by increasing the long-term test time. Their high catalytic activity and long-term durability at low temperature, low S/C ratio, and low gas flow rate need to be further demonstrated in a full-cell operation with a kinetics study,68,69 which will be performed in the following study.

5. Conclusions

In this study, we investigated Ni-based bimetallic alloy catalysts anchored on BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3-δ} (BZCYYb) which can be directly applied to the proton-conducting ceramic fuel cell (PCFC) anode for internal steam reforming of methane at low temperature. Maintaining the catalyst loading at 8 wt%, 8Ni, 6Ni2Rh, 6Ni2Co, and 6Ni2Cu (the number in front of the species name represents the metal loading in a mass basis) were considered as candidate materials. Characterization was carried out to confirm the structural properties and the formation of alloyed catalysts. The BET and CO pulse chemisorption analyses showed the coherent structural properties (i.e., specific surface area, metallic particle diameter, metallic surface area, and metal dispersion) of all catalysts, providing the same basis for a catalytic activity test. The XRD analysis confirmed the alloy formation of 6Ni2M (M: Co, Cu, Rh) catalysts by observing the peak of a 6Ni2M catalyst existing between the 8Ni and 8M peaks. TEM image analysis confirmed again their alloy formation and demonstrated nano-sphere particles anchored on the BZCYYb support. The TPR analysis revealed that the reducibility of 6Ni2M catalysts was improved compared to that of 8Ni.

The catalytic activities and long-term stability of 8Ni and 6Ni2M catalysts were evaluated for the internal steam reforming of methane at low temperature under various conditions (*e.g.*, operating temperature, steam-to-carbon ratio, and gas flow rate). 6Ni2Rh exhibited the highest catalytic activity at all temperatures given its low activation energy. The methane conversion and hydrogen yield of 6Ni2Co and 6Ni2Cu were lower than those of 8Ni due to their high activation energy for the onset of steam reforming. 6Ni2Rh's catalytic activity remained strong at various steam-to-carbon ratios. Its high activity was more evident at a high steam concentration due to its resistance to oxide formation. Lowering the steam-to-carbon

ratio improved 6Ni2Co's catalytic activity. Decreasing the steam concentration in the PCFC anode is desirable from the perspective of system efficiency and BZCYYb stability, which implies the feasibility of 6Ni2Co as a reforming catalyst in direct methane-fueled PCFC anodes. The high catalytic activity of 6Ni2Rh and 6Ni2Co at low temperature and low steam-tocarbon ratio makes them less dependent on the feed gas flow rate and gas hourly space velocity. Maintaining the high catalytic activity at various anode gas flow rates is critical for accounting for the variation of electrical demand, which implies the feasibility of 6Ni2Rh and 6Ni2Co as good reforming catalysts in PCFC anodes. They also showed higher resistance to carbon formation and stability in comparison with 8Ni, confirming again their feasibility as catalysts in direct methanefueled PCFC anodes.

6. Author contributions

Kyungpyo Hong: conceptualization, methodology, investigation, formal analysis, writing – original draft. Stephanie Nadya Sutanto: methodology, investigation. JeongA Lee: methodology, investigation. Jongsup Hong: supervision, writing – review & editing, project administration.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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