[Review Paper]

Materials and Systems Design for Energy Conversion with CO₂ Separation and Utilization Using Chemical-looping Technology

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To achieve net-zero CO₂ emissions over the coming decades, innovative new technologies, including separation, storage, and utilization of CO₂, are indispensable. Chemical looping technology may provide effective solutions and promising energy conversion systems for power plants and industrial applications with inherent CO₂ capture, avoiding energy penalties. Combined with appropriate CO₂ storage and utilization options, chemical looping can achieve net-zero emissions. The challenges, benefits, and prospects of chemical looping systems with various oxygen carriers and reactor configurations are discussed in this review to provide insights into the development of innovative systems in terms of solid looping materials, reactions, systems, and economics.

Keywords

Chemical looping, Circulating fluidized bed reactor, CCS, CCUS, Hydrogen production, Zero emission

1. Introduction

The latest report of the Intergovernmental Panel on Climate Change (IPCC) has provided unequivocal evidence that human influence has warmed the atmosphere, ocean, and land, and demands further reduction of CO₂ emissions¹⁾. Therefore, innovative new technologies, including separation, storage, and utilization of CO₂, are indispensable for achieving net-zero emissions by 2050.

Chemical looping (CL) technologies have the potential for reducing CO₂ emissions worldwide. The basic concepts of chemical looping combustion (CLC) processes²⁾ were presented in a patent by Lewis and Gilliland in 1954³⁾. The term “Chemical-Looping Combustion (CLC)” was first proposed by Ishida *et al.* in a thermodynamic study⁴⁾. The main features of CL systems are sequential redox reactions and CO₂ separation using multi-reactor systems with circulating metal oxide particles acting as oxygen carriers (OCs). The redox cycles form CO₂, H₂, and N₂ separately in each reactor as well as generate high-grade heat. Consequently, CL systems can separate CO₂ and reduce CO₂ emissions. Therefore, redox reactions involving metal oxides are important for application to CL systems in power generation, hydrogen production, and energy storage^{5)~7)}.

Various CL systems are shown in **Fig. 1**. In a typical CL system, the OCs circulate between the fuel reactor (FR) and the air reactor (AR), *i.e.*, the OCs are reduced (Eq. (1)) and reoxidized (Eq. (2)) repeatedly. During these reactions, carbonaceous fuels (C_mH_n) are converted to CO₂ in the FR and generate high-grade heat in the AR to produce electricity using a steam turbine, as shown in **Fig. 1(a)**. A CL hydrogen production system with CO₂ separation using three reactors was proposed for partially oxidizing OCs with steam to form H₂ (Eq. (3)), as shown in **Fig. 1(b)**. In addition, an advanced CL system involving energy conversion and storage with a reversible solid oxide fuel cell/solid oxide electrolytic cell (SOFC/SOEC) system, the CL-type air battery, has been proposed, as shown in **Fig. 1(c)**. The H₂-H₂O system acts as a redox mediator (Eq. (3))^{8),9)}.

(M: Fe, Ni, Cu, Mn etc.)

This review discusses the various CL and related technologies considering the material design of OCs and system design for CL combustion, hydrogen production, and energy storage systems investigated by our research. In addition, a techno-economic analysis of

Fig. 1 Schematic Diagrams of CL Energy Conversion Systems: (a) two reactor system, (b) three reactor system for hydrogen production, (c) CL air battery with SOFC/SOEC system

CL systems is discussed to promote future use of CL technologies. This review article consists of three sections: (1) material design of OCs and their redox kinetics, (2) diversity of CL systems design, and (3) techno-economic analysis of CL systems.

2. Materials Design of Oxygen Carriers and Redox Kinetics for CL Systems

2.1. Redox Kinetics Promotion by Ionic and Electronic Transport

Efficient OCs are critical for improving and diversifying the functions of CL systems. The characteristics required for functional OCs are rapid redox kinetics, durability for redox cycles, low cost, easy treatment of used material, environmentally friendly material, and rich natural resources with a large Clarke number. Therefore, natural ores are preferred, but artificial OCs are being developed incorporating fast redox kinetics, resulting in reduced reactor size. Therefore, developing multifunctional OCs is crucial. Redox reactions involving various metal oxides such as Fe_2O_3 , NiO ,

Fig. 2 Concept of Improving Redox Kinetics of OCs with Oxide Ion Conductor or MIEC as a Support
The figure was partially modified²⁵⁾. Reprinted/adapted from ref. 25) with permission from Elsevier.

MnO , and CuO have been investigated^{10)~16)}. Support materials can influence the physicochemical characteristics such as dispersability, durability, conversion, and selectivity. Thus, a variety of support materials such as Al_2O_3 , ZrO_2 , SiO_2 , TiO_2 , spinel (MgAl_2O_4 , NiAl_2O_4), and perovskite (*e.g.*, $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$) have been investigated^{17)~23)}. More information about previous studies on OC materials is collected elsewhere^{5),24)}.

Our concept to improve the redox kinetics of OCs is based on incorporating ionic and electronic conduction into the surface and interfacial redox reactivity of OCs by utilizing oxide ion conductors (OICs) and mixed ionic-electronic conductors (MIECs) as support materials as illustrated in **Fig. 2**. This concept is simple but very effective as shown below. Oxide ions can diffuse through the oxygen vacancies ($\text{V}_\text{O}^\bullet$) in oxide ion conductors and promote the redox kinetics of metal oxides at the interface between the oxide ion conductor and the metal oxide²⁵⁾. Electrons can diffuse together with the oxide ions in MIECs, so the transport properties of MIECs can promote the redox kinetics of metal oxides. **Table 1** lists the OCs developed in our previous studies.

Figure 3 shows the reduction and oxidation kinetics of various OCs using thermogravimetric analysis (TGA). Artificial OCs, particularly OCs with OIC and MIEC supports, showed faster reduction rates (*i.e.*, oxygen release rates in reduction reaction with dry methane) compared to natural ores such as ilmenite and iron ore (**Fig. 3(a)**). In this case, the specific surface areas of OCs were mostly the same ($1\text{--}4\text{ m}^2/\text{g}$). Thus, our results suggest significant improvements for OCs with OIC and MIEC supports. Yttria-stabilized zirconia (ZrO_2)_{0.9}(Y_2O_3)_{0.1} (YSZ) is an OIC and iron-doped calcium titanate $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_3$ (CTFO) is a MIEC, in which oxide ions can diffuse *via* oxygen vacancies in the crys-

Table 1 List of OCs Developed in Our Previous Studies

Oxygen carrier	Support	Support property	Ref.
Fe ₂ O ₃	Al ₂ O ₃	Insulator	26, 27, 28, 29
NiO	ZrO ₂	Insulator	25, 30
NiO, Fe ₂ O ₃	(ZrO ₂) _{0.9} (Y ₂ O ₃) _{0.1}	OIC	28, 30, 31
NiO, Fe ₂ O ₃	Ce _{0.9} Gd _{0.1} O _{2-δ} (GDC)	MIEC	25, 30
Fe ₂ O ₃	CaTi _{0.8} Fe _{0.2} O _{3-δ} (CTFO)	MIEC	26, 28
NiO	La _{0.9} Sr _{0.1} AlO _{3-δ} (LSA)	OIC, NP	25
Fe ₂ O ₃	BaZr _{0.9} Y _{0.1} O _{3-δ} (BZY)	PC, NP	32, 33
Ilmenite (Fe ₂ TiO ₅)	-	Insulator	34, 35
Ca-modified ilmenite (Fe ₂ TiO ₅ + CaTi ₁₋₃ Fe ₄ O _{3-δ} (CTFO))	-	MIEC	34, 35

MIEC: oxide ionic and electronic conductor, OIC: oxide ion conductor, PC: proton conductor, NP: exsolution of nanoparticle.

Spg: spray granulation method; Imp: impregnation method.

Fig. 3 Redox Kinetics of Fe with Various Supports for (a) Reduction Rate (oxygen release rate per unit OC mass) with 5 % Methane at 1173 K^{(26)~(29), (34)} and (b) Oxidation Rate (hydrogen formation rate per unit OC mass) at 873 K⁽²⁸⁾

Fig. 4 Oxidation (hydrogen production) Rate Constant as a Function of Oxide Ion Conductivity for the Different Supports⁽³⁰⁾ Reprinted from ref. 30) with permission from Elsevier.

tal lattice. Electrons and holes also diffuse together with the oxide ions in CTFO. These transport properties will improve the reduction kinetics^{(26), (28), (30), (31), (33)~(35)}. We also observed remarkable promotion of oxidation reaction, *i.e.*, hydrogen formation reaction with steam by CTFO supports as shown in **Fig. 3(b)**^{(28), (30)}. Promotion of oxidation kinetics as well as improvement of reduction kinetics were also observed using other MIECs such as gadolinium-doped ceria Ce_{0.9}Gd_{0.1}O_{2-δ} (GDC)^{(25), (30)}.

Figure 4 shows the relationship between the oxide ion conductivity of these carrier materials and the oxidation reaction rate constant of iron oxide, calculated using the Avrami-Erofeev equation. The oxide ion conductivity of the support materials showed a remarkable correlation with the reaction rate. This indicates that oxide ion transport *via* the carrier contributed to the reaction promotion⁽³⁰⁾.

Additionally, the correlation between the redox kinetics and the OC microstructure was investigated with backscattered electron imaging (BEI) to investigate the microstructures of Fe₂O₃/GDC. **Figure 5** shows the cross-sectional BEI of the Fe₂O₃/GDC composite parti-

Fig. 5 Image Analysis of Cross-sectional BEI of $\text{Fe}_2\text{O}_3/\text{GDC}$ Composite Particle³⁶⁾
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Fig. 6 (a) Arrhenius Plot of k for the Reduction of $x\text{Fe}_2\text{O}_3-(1-x)$ GDC ($x = 30, 50, 70, 90$ vol%), $50\text{Fe}_2\text{O}_3-50\text{Al}_2\text{O}_3$, (b) Apparent Activation Energy for the Reduction of Fe_2O_3 -GDC Plotted against the Apparent Length of the Phase Boundary between Fe_2O_3 and GDC³⁶⁾

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cle; white, gray, and black areas correspond to GDC, Fe_2O_3 , and pores, respectively³⁶⁾. The apparent phase boundary lengths between Fe_2O_3 and GDC were evaluated by image processing of the BEI. The reduction kinetics were correlated with the apparent phase boundary lengths. The apparent activation energy for the reduction of $\text{Fe}_2\text{O}_3/\text{GDC}$ monotonously decreased with greater apparent phase boundary length as shown in

Fig. 7 Oxygen Transport Modeling of Fe_2O_3 Reduction with Oxide Ion Conductor Support²⁸⁾

Fig. 6, indicating that promotion of Fe_2O_3 reduction may occur at the two-phase and three-phase boundaries in $\text{Fe}_2\text{O}_3/\text{GDC}$ ³⁶⁾. Additionally, oxygen desorption at the phase boundary between Fe_2O_3 and GDC may occur, which also promotes the reduction kinetics.

2. 2. Model Description of Redox Kinetics Promotion with Oxide Ion Transport at the Metal Oxide and Ion Conductor Interface

To further evaluate the promotion of the redox kinetics of OCs discussed above, the involvement of oxide ion transport was investigated based on the oxygen potential distribution in the particles (Eq. (4)). This mechanism may explain the process of redox kinetics promotion and provide guidelines for further improving these redox reactions²⁸⁾.

$$J_o = -\frac{\sigma t_o(t_e + t_h)}{z_o^2 F^2} \nabla \mu_o \quad (4)$$

where oxygen flux J_o is determined by transport properties such as conductivity σ , transport number t_i for species i (o : oxide ion, e : electron, and h : hole), and gradient of oxygen chemical potential μ_o . z_o and F are the charge number of oxygen and the Faraday constant, respectively.

The model was based on the reduction reaction kinetics on the particle surface and oxide ions diffusion due to the gradient of the oxygen chemical potential in OC particles (Eq. (4)). The spatial distribution of the reaction promotion near the support and iron oxide interface was evaluated (Fig. 7). The model calculation indicated that the reduction rate improved with higher oxide ionic conductivity in the support, whereas a smaller increase in the reduction rate was obtained with higher electronic conductivity. The results demonstrate that the effect of oxide ionic conductivity is predominant, but electronic conductivity also contributes to improving the reduction kinetics. Thus, the kinetic improvements by YSZ and CTFO are largely comparable, despite the high electronic conductivity of CTFO²⁸⁾. Conversely, the experimental results for oxidation (H_2 evolution) with CTFO suggest that the oxidation kinetics are strongly influenced by both the oxide ionic and electronic conductivity, indicating that CTFO has

Cross-sectional BEI (a) before and (b) after redox cycles²⁹.

Fig. 8 Coarsening of Fe Particles Inside the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ Particle (Reprinted/adapted with permission from ref. 29). Copyright 2018 American Chemical Society.

well-balanced properties for redox kinetics. Therefore, the transport properties of CTFO were applied to Ca-modified ilmenite as a novel OC.

2. 3. Structural Stability in OCs during Redox Cycles due to Ionic and Electronic Transport Properties

Oxide ion transport may also contribute to the structural stability of OCs during redox cycles and promote redox kinetics. Microstructural changes in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, a standard artificial OC, were investigated during redox cycles using an image analysis method of cross-sectional backscattered electron images²⁹. Coarsening of Fe particles inside the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ particles was observed for 25 wt% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, whereas Fe segregation at the surface and coarsening of Fe particles inside the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ particles were observed for 50 wt% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ as shown in Fig. 8. The redox kinetics slowed due to the reduction in the specific surface area of Fe associated with the coarsening of Fe particles.

Ilmenite (IL: FeTiO_3) was introduced to improve the redox kinetics and suppress the morphological changes during redox cycles. IL is a natural ore and a typical OC used in actual CL systems. IL was modified through the impregnation method with a calcium additive to form CTFO on the ilmenite surface and interior (Ca-modified ilmenite: Ca-IL). Consequently, a structure with an ilmenite core and CTFO shell was formed³⁴. The production process of Ca-IL was also investigated using the melt-infiltration method to deeply penetrate Ca in Ca-IL³⁵. Cross-sectional scanning electron microscope (SEM) images of the modified and unmodified ILs are shown in Fig. 9. In unmodified IL, Fe migrates toward the surface and forms an Fe-rich layer after redox cycling. This tendency induces decomposition to form powdered microparticles and particle aggregation. The ilmenite particles will experience reduced lifetime in redox cycles. Conversely, Ca-IL prepared by the impregnation method indicated Ca modification around the particle surfaces, forming grains rich in Ca and Ti close to the surface; *i.e.* a CTFO surface layer was formed. In addition, Ca-IL prepared by the melt-infiltration method exhibited improved penetration of Ca into the particles. After

Grayscale images: Backscattered Electron Image (BIE) analysis. Colored images: EDX mapping. Top left: unmodified ilmenite (IL) after calcination in air. Bottom left: neat IL after redox cycling after calcination in air. Top right: melt-infiltrated Ca-modified ilmenite (Ca-IL). Bottom right: Ca-IL after redox cycling³⁵.

Fig. 9 SEM-EDX Cross-sectional Analysis (Reprinted/adapted with permission from ref. 35) under the terms of CC BY-NC-ND 4.0 license.

redox cycling, Fe segregation on the surface did not occur in the Ca-ILs, and the structure of Ca- and Ti-rich grains throughout the particles was maintained for Ca-IL prepared by the melt-infiltration method, in contrast to the Ca-rich surface layer formation for Ca-IL prepared by the impregnation method. Furthermore, the use of modified ilmenites improved the reduction kinetics in dry H_2 and wet CH_4 (*i.e.*, humidified condition: steam to carbon ratio = 2). The kinetic improvement was due to the formation of CTFO in Ca-IL. Therefore, the interface of the CTFO grains may promote redox kinetics together with $\text{Fe}_2\text{O}_3/\text{CTFO}$.

Figure 10 shows the mechanism of cation diffusion in Ca-IL³⁴. Significant Fe surface segregation and formation of a porous structure in unmodified IL were observed during redox cycling, which will shorten the lifetime of the OCs. The diffusivity of the oxide ion is lower than that of the reduced iron cation in unmodified IL. In addition, the oxygen potential gradient along the surface to the center of the particle is relatively large during the oxidation process, because of the low diffusivity of the oxide ion. Therefore, the reduced iron cation diffuses toward the IL particle exterior according to the oxygen potential gradient, before iron oxidation occurs at the surface. The iron cation is then easily transported toward the particle exterior, and Fe segregation occurs at the surface of the unmodified IL particle (Fig. 10(a)). In contrast, fast oxide ion transport into

ilmenite is the dominant oxidation step in Ca-IL, *i.e.*, fast oxide ion diffusion toward the IL particle interior occurs according to the oxygen potential gradient, and this phenomenon can suppress the outward diffusion of iron ions (**Fig. 10(b)**). Ilmenite modification with CTFO can provide high redox reactivity and suppress the outward diffusion of iron cations and resultant morphological changes, extending the lifetime of OCs during redox cycles.

3. CL Systems Design for a Variety of Carbonaceous Fuels and CO₂ Utilization

3.1. CL Systems Design

CL technology flexibly facilitates a variety of reactions using a combination of redox reactors. The following CL systems were investigated: (a) Conventional redox system with fuel and air reactors (**Fig. 1(a)**), (b) hydrogen production system using steam reforming

Fig. 10 Schematic Diagram of Redox Reaction and Morphological Changes for (a) Unmodified and (b) Ca-modified Ilmenites during Redox Cycles

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with reforming and air reactors (*i.e.*, using FR and AR in **Fig. 1(a)**)^{5),10),37)}; (c) hydrogen production system using steam-iron reaction with fuel, steam, and air reactors (**Fig. 1(b)**), and other applications such as (d) air battery system with a steam reactor and SOFC/SOEC (**Fig. 1(c)**); and (e) CO₂ utilization systems for CO and syngas production with two or three reactors^{32),33)}. Various carbonaceous fuels have been investigated for CL systems such as coal, petroleum, natural gas, and woody biomass^{5),37)}. Additionally, solar-thermochemical water splitting with metal oxides has been investigated in combination with renewable energy^{40),41)}. A brief list of CL systems is provided in **Table 2**.

3.2. Demonstration of 100 kW CLC Pilot Plant

To scale up CL systems, national projects supported by the New Energy and Industrial Technology Development Organization (NEDO) in Japan have demonstrated a 100 kW-class CLC pilot plant operation^{42),43)}. A 100-kW circulating fluidized bed system with three reactors was built, and CLC operations were carried out using solid fuel. The CLC system consisted of (1) riser: air reactor (AR), (2) carbon (coal) reactor (CR): 1st stage fuel reactor, and (3) volatile reactor (VR): 2nd stage fuel reactor, as shown in **Fig. 11**. This project evaluated coal combustion using the CLC system with natural ilmenite as OC.

The demonstration project achieved stable operation during continuous coal feeding. Overall, the CO₂ capture rate from the VR was 74 %, 9 % of CO₂ was released from the AR, and 13 % of the residue was soot from the VR⁴²⁾. Thus, the CO₂ capture rate (74 % in the VR) can be improved by reducing the amounts of soot and char in the CR and prevention of transfer to the AR by adjusting the operating conditions. We restarted a follow-up project of polygeneration of H₂, CO₂, and N₂ based on woody biomass fuel, using a CL steam-ion reaction supported by NEDO in 2020⁴⁴⁾. Because the system developed in this project includes a

Table 2 List of Various CL Systems

System	Reactor configuration	Fuel	Ref.
Combustion, power plant with CCS			
CL combustion	AR, FR	coal, LNG, petroleum, biomass	5, 37, 38
Syngas, hydrogen production with CCS			
CL reforming	AR, FR	coal, LNG, petroleum, biomass	5, 10
CL steam-iron reaction	AR, FR, SR	coal, LNG, biomass	5, 24, 28
Advanced energy storage			
MO-redox type air battery	SR, fuel cell	H ₂ , H ₂ O	8, 9, 28
CO₂ utilization for CCUS			
CL CO production	FR,	coal, LNG, biomass with CO ₂	39
CL methane cracking	cracker, regenerator	LNG with CO ₂	34, 35
CL methanation for DAC	carbonator, methanator	coal, LNG, biomass with CO ₂	32, 33
Solar thermochemical splitting of H₂O and CO₂ for CCUS			
MO-redox type solar thermochemical splitting	solar collector, cavity receiver	coal, LNG, biomass with CO ₂	40, 41

AR: air reactor, FR: fuel reactor, SR: steam reactor, DAC: direct air capture, MO: metal oxide.

Fig. 11 A 100 kW Circulating Fluidized Bed (CFB) CLC System with Three Reactors⁴²⁾
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hydrogen production process, OCs with fast redox kinetics and long-term durability in redox cycles are required to reduce reactor size and operation costs. Additionally, our studies on OCs will contribute to the development of new CLC systems.

3.3. CCUS Systems Design with CL Technology

CL technologies are suitable for carbon dioxide capture, utilization, and storage (CCUS) based on the CO₂ circular economy. The following reactions are available to activate CO₂ and its effective use:

In Eq. (5), CO₂ methanation, the famous Sabatier reaction, is crucial because the power-to-gas concept provides the perspective of large-scale circulation of CO₂ emissions combined with the use of renewable energy to form methane⁴⁵⁾. CL can be combined with CO₂ capture and methanation processes (**Fig. 12(a)**). CO₂ capture with CL has been investigated using a carbonation/decarbonation cycle of calcium looping with CaO and CaCO₃⁴⁶⁾. By combining the CO₂ capture process (Eq. (8)) with methanation (Eq. (9)), a combined system of CO₂ separation and methanation can be designed, as shown in **Fig. 12(a)**. CO₂ is separated from flue gas or air; *i.e.*, direct air capture (DAC), in a carbonator. Methane then forms due to CaCO₃ reacting with hydrogen during methanation⁴⁷⁾.

Ru and Ni catalysts can be used for CL methanation^{48,49)}. We also established that Ni catalyst support-

Fig. 12 Schematic Diagrams of (a) CL Methanation, (b) CO Production with RE, (c) CO Production with Methane Cracking

ed by proton conductors such as yttrium-doped barium zirconate (BZY) is highly active in the cyclic process⁵⁰⁾. We also proposed CO₂ activation with hydrogen produced by renewable energy (RE) such as solar cells and methane cracking to produce CO from CO₂, as shown in **Fig. 12(b)**³⁹⁾. The OC is reduced by hydrogen produced by RE *via* water electrolysis, and CO₂ reacts with the reduced OC to form CO. In this process, the CO concentration and energy conversion efficiency have a trade-off relationship. We discussed the appropriate OC materials based on thermodynamics to determine the best choice for each combination of CO concentration and efficiency, *i.e.*, the Pareto front of CO concentration and efficiency was discussed³⁹⁾. In another process, we proposed CO₂ activation combined with methane cracking to produce H₂ and CO, as shown in **Fig. 12(c)**^{32,33)}. A proton conductor (Fe-doped BZY: BZFY) was used as the OC in this reaction. The kinetic analysis indicated high activity for carbon deposition *via* methane cracking and the resultant promotion of tubular carbon growth on BZFY³³⁾. In the reduction step, an exsolution of Fe nanoparticles occurred on the BZFY surface (see **Fig. 13(a), 13(b)**). The rapid growth of carbon tubes proceeded with the base-growth mechanism, *i.e.*, carbon tubes grew on the Fe particles anchored on BZFY (see **Fig. 13(c), 13(d)**), which is advantageous for stable redox cyclic reactions. Addi-

Fig. 13 (a) SEM Image of BZFY Surface, (b) EDX Analysis of Fe on BZFY, Bright Color Circles Suggest Fe Nanoparticle Exsolution, (c) Carbon Nanotube Growth on Anchored Fe Particles (red circles), (d) Enlarged Image of Carbon Nanotube Growth

Fig. 14 Material and Heat Flows in the SOFC Combined System for CO Production with Methane Cracking (modified figure in the SI³³⁾)
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tionally, the carbon removal reaction with carbon dioxide (Eq. (7)) proceeded quickly. Based on these findings, a new chemical looping system was proposed in combination with an SOFC system (Fig. 14). Assuming that the waste heat of the SOFC system and the heat of CH₄ off-gas combustion from the cracker are used for the endothermic reactions of methane cracking and carbon removal, a self-sustained operation is possible. Therefore, the proposed system provides an effective system design for carbon dioxide-free hydrogen generation.

3. 4. Techno-economic Analysis of CL Systems

To investigate the potential widespread uses of CL technologies, integrated approaches combining technological and economic assessments were conducted.

Fig. 15 Costs of CO₂ Avoided for Different Technological Options for Reducing CO₂ Emissions⁵¹⁾
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Japanese woody biomass energy (BE) for negative emissions *via* thermal power plants and subsequent carbon dioxide capture and storage (BECCS) has been investigated^{51),52)}. In this study, a novel unmixed combustion technology, CLC with woody biomass (BE-CLC) was benchmarked in comparison with a conventional BE process with post-combustion CO₂ capture; *i.e.*, the conventional circulating fluidized bed combustion (CFBC) process using woody biomass fuel in combination with post-combustion amine scrubbing (CFBC-CCS). The analysis was conducted based on the detailed modeling of fluidized-bed CLC reactors with different fuel input scales. The use of CLC saved up to 17 % of the total BECCS cost per tonne of CO₂ captured. The analysis also suggested that the cost-optimal plant size was 5 MWth in Japan⁵²⁾. However, the CO₂ capture cost remained over US\$160/t-CO₂ because of high fuel costs. This cost can be reduced to US\$130/t-CO₂ with reduction in the fuel cost from US\$200/dry tonne to US\$100/dry tonne⁵¹⁾. Despite the high fuel cost of Japanese woody biomass, CLC-CCS may be the cheapest CO₂ abatement option compared to coal combustion with CCS, CFBC-CCS, solar cells, and wind farms, if the average CO₂ intensity of the replaced generation capacity is below 0.35 kgCO₂/kWh (*cf.* the average value of the current Japanese grid is approximately 0.53 kgCO₂/kWh) (Fig. 15). Therefore, CLC is an effective option for reducing CO₂ emissions. If economic incentives such as carbon pricing are introduced to encourage the reduction of CO₂ emissions, CL technology can demonstrate its technological advantages for separating and utilizing CO₂.

4. Conclusion

Various CL systems will emerge from the development of reactor configurations and solid looping materi-

als and provide innovation pathways for novel energy conversion systems to achieve zero CO₂ emissions over the coming decades. CL can achieve net-zero emissions of CO₂ combined with CCS and CCUS. The OCs in CL systems are the key materials for determining the system performance, effective energy conversion, and CO₂ separation. The transport properties of OCs controlled using a range of MIECs achieve fast redox kinetics. Oxide ion and proton conductors performed well in terms of redox kinetics and methane cracking. MIECs improve both the redox kinetics and the durability during redox cycles. Calcium-modified ilmenite showed good morphological stability as well as fast redox kinetics, which were caused by the formation of MIEC domains in the particles. Thus, OC material design based on MIECs is promising.

System design and scale-up of CL plants have also advanced. A 100 kW CLC operation with coal combustion was built as a CLC demonstration of a pilot plant with three reactors (VR, CR, and AR), and operated using a natural ilmenite for the solid looping material in a national project. The demonstration proved stable operation with continuous feeding of coal. This technology has been installed in a subsequent project with poly-generation of H₂, CO₂, and N₂ with the CL steam-ion reaction using woody biomass solid fuels. To apply CL to CCUS, the CO₂ activation process was also investigated. CO production and methanation using DAC systems have been proposed. These systems possess the potential for net zero and net negative emissions of CO₂.

Techno-economic analysis of BECCS was conducted, considering net negative emissions. CLC-CCS has the potential to be the cheapest CO₂ abatement option, compared with other options such as conventional BECCS and renewable energies if the average CO₂ intensity of the generation capacity is below 0.35 kgCO₂/kWh. Thus, CL technologies will demonstrate their advantages for the separation and utilization of CO₂ in the near future.

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要 旨

ケミカルループ法に基づく二酸化炭素分離・利用型エネルギー変換技術の材料およびシステム設計

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今後数十年で二酸化炭素の正味の排出量ゼロ（ゼロ・エミッション）を達成するには、二酸化炭素の分離、貯蔵、利用などの革新的な新技術の開発が必要不可欠である。ケミカルループ法は、追加のエネルギー投入を必要としない二酸化炭素分離型の発電技術で、二酸化炭素を化学原料に変換する効率的なエネルギー変換システムや産業応用を提供する技術である。適切な二酸化炭素の貯留と利用技術を組み合わせることで、ケミカル

ループ法を用いたゼロ・エミッションが達成可能である。本総合論文では、ケミカルループシステムの循環媒体である酸素キャリア粒子の材料開発や複数の反応器から構成されるシステム設計について、著者らの研究を中心に、開発の課題、利点、および今後の展望について述べ、材料、反応、システム、および経済性の観点からケミカルループシステムの最新の動向について解説する。

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