New developments and challenges of solid oxide fuel cell (SOFC) – based technologies

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Solid oxide fuel cells (SOFCs) are promising electrochemical devices for efficient energy conversion using various alternative fuels, such as H_2, natural gas, biogas, ammonia, and solid carbon. In recent years, significant progress has been made in SOFC with proton conducting electrolyte and direct carbon SOFC. In addition to power generation, SOFC-based technology can be applied in different areas, including electrolysis for energy storage, oxygen separation, nitrogen oxides removal, and electrochemical NH_3 synthesis. In this perspective, the different SOFC-based technologies will be summarized and the challenges will be discussed.

1. Oxygen ion conducting electrolyte versus proton conducting electrolyte

SOFCs can be based on oxygen ion conducting electrolyte, such as YSZ, LSGM, GDC, etc, or proton conducting electrolyte, such as BZCY (Figure 1). The proton conducting SOFC is promising for intermediate temperature (400-600°C) operation due to higher ionic conductivity of the proton conducting electrolyte such as BZCY than almost all oxygen ion conducting electrolytes. Although proton conducting SOFC can only electrochemically oxidize H_2 fuel, hydrocarbon fuels can be used as well since H_2 can be obtained from hydrocarbon steam reforming [1,2]. Despite great potential for intermediate temperature applications, significant research efforts on proton conducting SOFCs are needed to fabricate larger-scale, low cost, fuel flexible and stable SOFCs with thin and dense proton conducting electrolyte.

2. In addition to gaseous fuels, solid carbon can be used in SOFC for power generation. The use of solid carbon fuel is very meaningful, as carbon is a major component of coal and can be derived from biomass as well. As the size of the solid carbon particles is usually much

larger than the pore size of the SOFC anode, the solid carbon fuel cannot reach the triple phase boundary (TPB) through the porous anode layer. Therefore, the operation of direct carbon SOFC (DC-SOFC) relies on the reversible boudouard reaction: $C + CO_2 \leftrightarrow 2CO$ (Figure 2). The boudouard reaction help convert solid carbon fuel into CO, which diffuse from the carbon layer to the TPB in the porous anode to participate in the electrochemical reaction, from which the CO_2 is produced and diffused back to the carbon layer for continuous boudouard reaction. As the boudouard reaction rate is relatively slow, the operating temperature of DC-SOFC is usually above 850^oC, which is unfavorable for long-term operation. Recent modeling and experimental research demonstrated that carbon gasification by steam (instead of CO_2) can enable operation of DC-SOFC at a lower temperature of about 750^oC, due to faster steam carbon gasification reaction (Figure 2b) [3,4]. In addition, H_2 is generated from steam carbon gasification, which can be electrochemically oxidized more easily than that of CO. These features indicate that H_2O is a good gasification agent for DC-SOFC. To further improve the performance of DC-SOFC, developments of efficient catalyst to further enhance the carbon gasification reaction and stable anode materials for both H_2 and CO oxidation are needed. Another development in DC-SOFC is the use of liquid metal such as Sb as the anode, which ensures excellent contact between the carbon fuel and the anode [5]. However, as Sb oxidation is the anode half reaction, the open circuit voltage (OCV) of DC-SOFC based on liquid Sb anode is less than 0.7V [5], limiting the power output of the cell. Mixing the solid carbon fuel with carbonate at the anode side DC-SOFC could also ensure good contact between the anode and the carbon fuel, but the corrosion caused by the carbonate causes poor long-term durability of DC-SOFC [6]. The long-term durability is even more challenging when coal is used as a fuel for DC-SOFC, due to the poisoning effects of some impurities, such as sulfur.

3. The operation of SOFC can be reversed and the cell is called solid oxide electrolysis cell (SOEC) (Figure 3). The SOEC can be driven by excess renewable power to split H_2O

and CO_2 into H_2 and CO. When the renewable power is insufficient, the previously produced H_2 and CO fuel can be used in an SOFC for power generation. The reversible operation of SOFC/SOEC makes this technology suitable for large-scale electrical energy storage [7,8]. In addition, the produced H_2 and CO fuel can be further processed by a Fischer–Tropsch (FT) process to produce various valuable chemical products [9]. Thermodynamic analysis revealed that the optimized SOEC-FT system can achieve an overall efficiency of 66.67% with paraffins as the major yield [9]. Some researchers also tried to directly produce CH_4 from SOEC by H_2O/CO_2 co-electrolysis, but the CH_4 molar fraction in the gaseous product is below 1% at 750^oC [10]. To favor CH_4 production, lower temperature and higher pressure are needed. Prof. Changrong Xia et al., [11] designed an innovative reactor by integrating SOEC with a FT section in a single chamber with higher temperature in the SOEC section while lower temperature in the FT section (down to 250^oC). At an SOEC temperature of 800^oC, the CH_4 yield was significantly improved to 11.84%. Based on numerical simulation, it was found that the CH_4 conversion could be enhanced by 2.5 times by increasing the pressure to 3 bar [12,13]. It is expected that the SOEC-FT technology can be a promising option for valuable chemicals production using the excess wind or solar power.

4. The oxygen ion conducting electrolyte can be used for oxygen separation to obtain pure oxygen which has various applications [14]. When pure oxygen ion conducting membrane is used, an external circuit is needed to complete the process by transferring electrons from the pure oxygen side to the other side of the membrane (Figure 4a). With an externally applied voltage, it is possible to pump oxygen from the gas mixture with low oxygen partial pressure to the other side with higher oxygen pressure. Another strategy is to develop mixed ionic and electronic conducting membranes without external circuit (Figure 4b). Perovskite oxides such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $Ba_{0.3}Sr_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) have been developed and demonstrated to be promising for oxygen separation [15,16]. With a 1.5mm thick BSCF

membrane, a high oxygen permeation flux of 1.19ml/(cm^2 min) at 850°C was achieved [16]. In another study by Shao et al. [17], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane was fabricated for oxygen permeation and methane oxidation. With oxygen partial pressures of 0.21atm and 0.05atm at the two sides of the 1.5mm thick membrane, an oxygen permeation flux of 1.6ml/cm^2 min was achieved at 950°C. Recently, $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ)−$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF) composite membrane was developed for oxygen separation [18]. The composite membrane consists of a 150μm dense layer for oxygen permeation and a 850μm porous layer for mechanical support. To enable continuous operation without external circuit, the feeding air is usually pressurized to increase the oxygen partial pressure or a vacuum pump is used to drain off the permeated oxygen [19]. Alternatively, sweep gas such as steam can be used to take away the produced oxygen to reduce the oxygen partial pressure and pure oxygen can be obtained easily by condensing the steam.

5. Nitrogen oxides (NOx) are common pollutants from internal combustion engines or thermal power plants. In the urban areas, NOx removal is critical to reduce the emissions from vehicles. The SOEC-based technology can be used for NOx removal by selective electrochemical reduction. Since O_2, CO_2, and some H_2O are also present in the exhaust gas, O_2 permeation through the SOEC and H_2O/CO_2 co-electrolysis could happen simultaneously. Thus, NOx removal in the presence of O_2 is a combination of SOEC and O_2 permeation processes (Fig. 5). NO electrochemical reduction to N_2 was first demonstrated by Pancharatnam et al. [20] with YSZ electrolyte and Pt electrode. Later, the presence of O_2, H_2O and CO_2 in the exhaust gas is considered in NO removal by an SOEC with CeO_2-based electrolyte and Pd electrodes at 450-800°C [21]. It was found that the presence of H_2O and CO_2 could improve the conversion from NO to N_2. In a recent mechanistic modeling study, the effects of H_2O and CO_2 on NO removal was investigated [22]. Although H_2O and CO_2 electrolysis could take place and compete with NO electrochemical reduction, the produced H_2

and CO can help reduce NO to N_2 chemically, leading to higher NO conversion. However, the presence of O_2 is unfavorable for NO removal as O_2 reduction proceeds much faster on Ni, Au and Pt electrodes [23]. To improve the selectivity towards NO reduction, the use of NOx adsorption material (Ba, K et al.) in the cathode was proposed and demonstrated to be effective to improve NO conversion [24]. An electrochemical cell with $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) electrolyte and $(La_{0.85}Sr_{0.15})_{0.99}MnO_3$ (LSM) electrodes were developed for NOx removal under O_2-rich environment [25]. Good performance for NO conversion was found at 350-400°C and a low voltage (1.5-2.0V). However, the performance was poor at a higher voltage and higher temperature as the adsorption layer impeded the NO diffusion to the reaction sites. More recently, a novel system was developed by integrating a $La_{0.9}Sr_{0.1}CoO_{3\pm\delta}$ (LSC) layer with LSM/GDC cell with BaO nanoparticles [26]. NO is first oxidized by O_2 in the stream with the LSC catalyst, then the formed NO_2 is electrochemically reduced by the LSM/GDC -based SOEC. At 375°C and in an environment with 1000 ppm NO and 8% O_2, the novel system achieved a NOx conversion of 65-75% [26]. To further improve the performance of the system, design optimization is needed to enhance NOx diffusion, adsorption, and electrochemical reduction processes.

6. NH_3 is an important chemical for fertilizer industry and other chemical industry. The annual production of NH_3 is higher than 200 million tons [27]. NH_3 is synthesized by the Haber-Bosch process, which was developed more than 100 years ago. The Haber-Bosch process is done with Fe-based catalyst at 400-500°C, with a high pressure of about 150 bar and an equilibrium conversion of only about 15% [28]. In recent years, SOFC-based technology has been developed for NH_3 electrochemical synthesis at an atmospheric pressure (Figure 6). With a proton conducting electrolyte, NH_3 can be electrochemically synthesized from N_2 and H_2 or H_2O [28,29] (Fig. 6a and 6b). With $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) electrodes and BZCY electrolyte, the highest NH_3 synthesis rate was 8.5×10^{-11} mol cm^{-2} s^{-1} at 550°C [29]. With an oxygen ion conducting electrolyte, NH_3 is synthesized from N_2 and H_2O mixture, enable the

possibility of direct NH_3 synthesis from wet N_2 or even from wet air [30]. However, the rate of NH_3 electrochemical formation is usually at the order of $10^{-11} – 10^{-9}$ mol cm^{-2} s^{-1} at 400-600°C, which is still too low for commercial applications. It should be noted that H_2 could be formed in the electrochemical system if the applied voltage is relatively high (sufficient for hydrogen evolution reaction: HER). Thus, efficient catalyst with high selectivity towards NH_3 formation should be developed. In addition, as NH_3 can be decomposed at a high temperature, development of thin film electrolyte with high ionic conductivity at a lower temperature is important for NH_3 electrochemical synthesis at reduced temperature.

SOFCs are promising electrochemical device for efficient energy storage. The proton conducting SOFCs have demonstrated good performance and good durability at an intermediate temperature with hydrocarbon fuels. Efforts are needed to simplify the fabrication procedure of the electrolyte, especially for large-scale cells. DC-SOFCs demonstrated good performance at a temperature of below 800°C with H_2O as a gasification agent. Efficient catalysts are needed to facilitate carbon gasification and H_2/CO electrochemical oxidation. With further investigation, DC-SOFC could be a promising technology for direct coal utilization for power generation. SOECs are very promising for energy storage and CO_2 utilization. The H_2O/CO_2 co-electrolysis by an SOEC can be integrated with a F-T reactor to produce various valuable chemicals. The SOFC-based technology can also be applied for O_2 separation. With reduced electrolyte thickness and suitable catalyst, the O_2 separation can be realized with high efficiency. NOx removal is critical for pollutant emission reduction from vehicles. With an SOEC, NOx can be electrolytically decomposed to N_2 and O_2. Suitable catalyst and reactor design are required to remove NOx in the presence of O_2, H_2O and CO_2 at a temperature of 300-400°C. The SOEC technology can be used for electrochemical NH_3 synthesis at atmospheric pressure. Both proton conducting electrolyte and oxygen ion conducting electrolyte can be used. NH_3 can be synthesized from N_2 and H_2, N_2 and H_2O, or even directly from wet air. However, the rate of NH_3 synthesis is still too low to be practical. Significant efforts are needed to develop high performance catalyst with high selectivity towards NH_3 synthesis. With further development in materials science and engineering design, SOFC-based technologies could play an important role in energy conversion, storage, oxygen separation, NOx removal and NH_3 synthesis.

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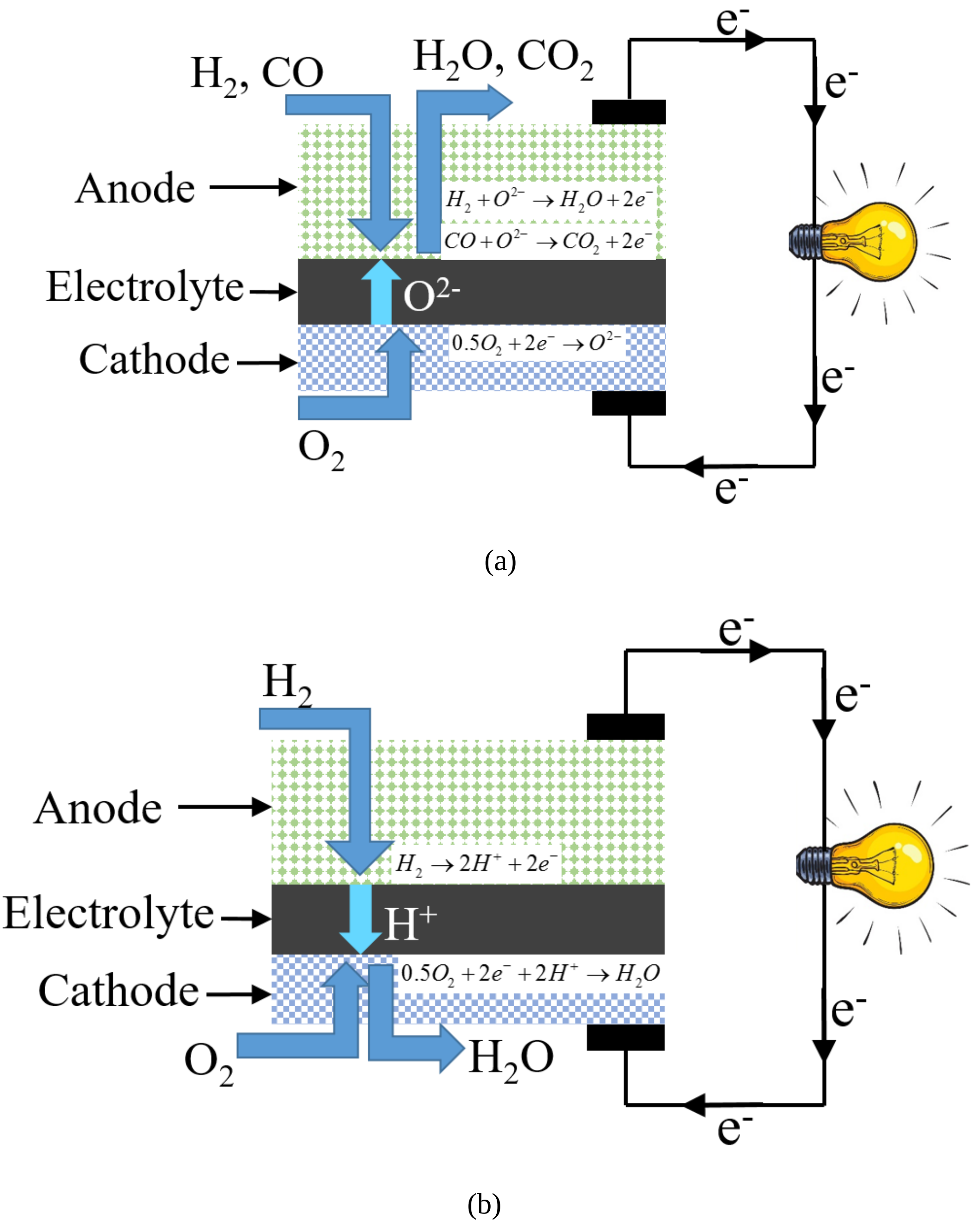
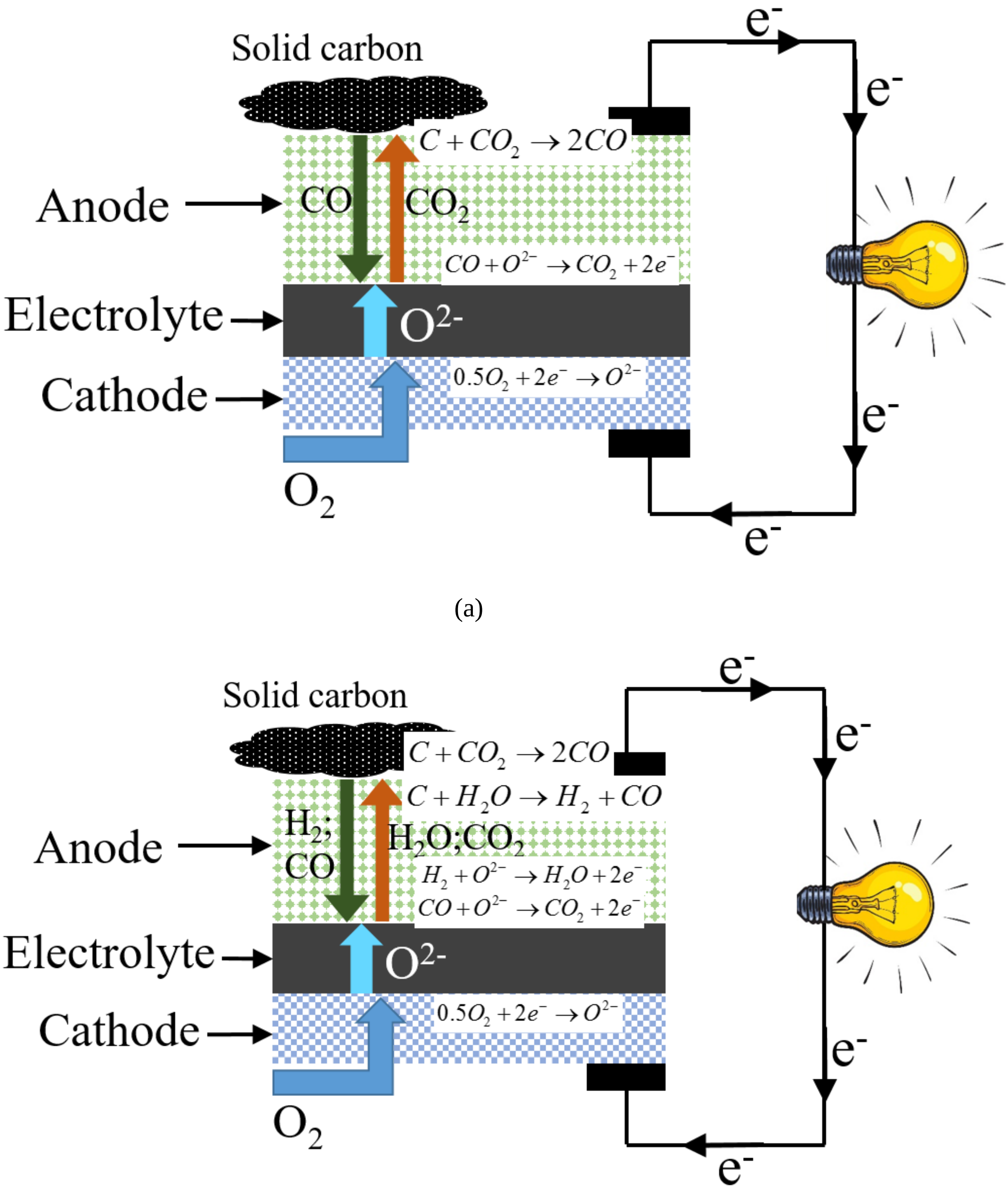


Figure 1. Working principle of SOFC based on: (a) oxygen ion conducting electrolyte; (b) proton conducting electrolyte



(a)

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Figure 2. Working principles of direct carbon SOFC (DC-SOFC): (1) Boudouard reaction for carbon gasification; (b) carbon steam gasification

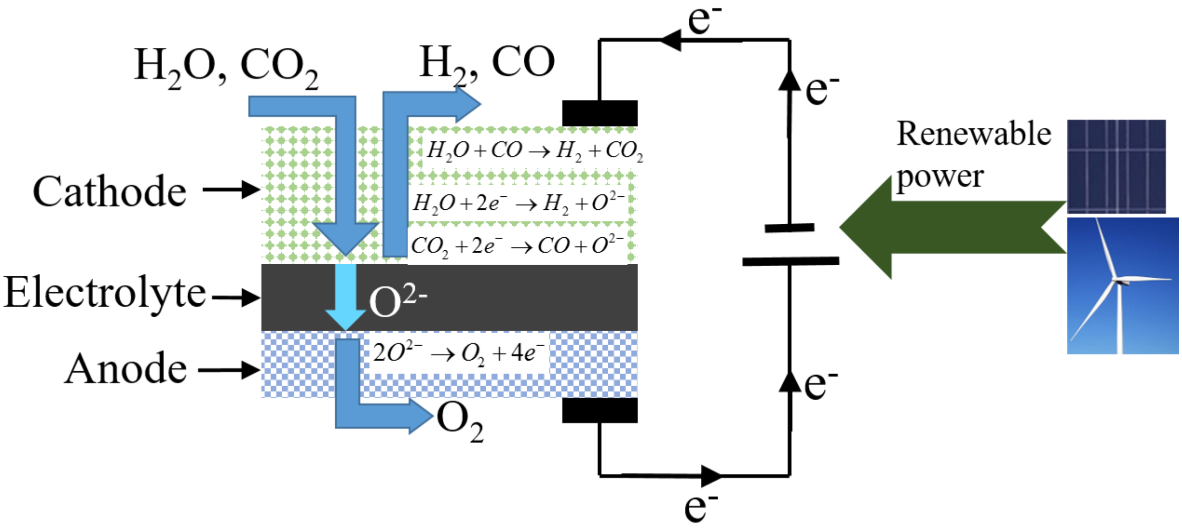

Figure 3. Operation of solid oxide electrolysis cell (SOEC) for energy storage

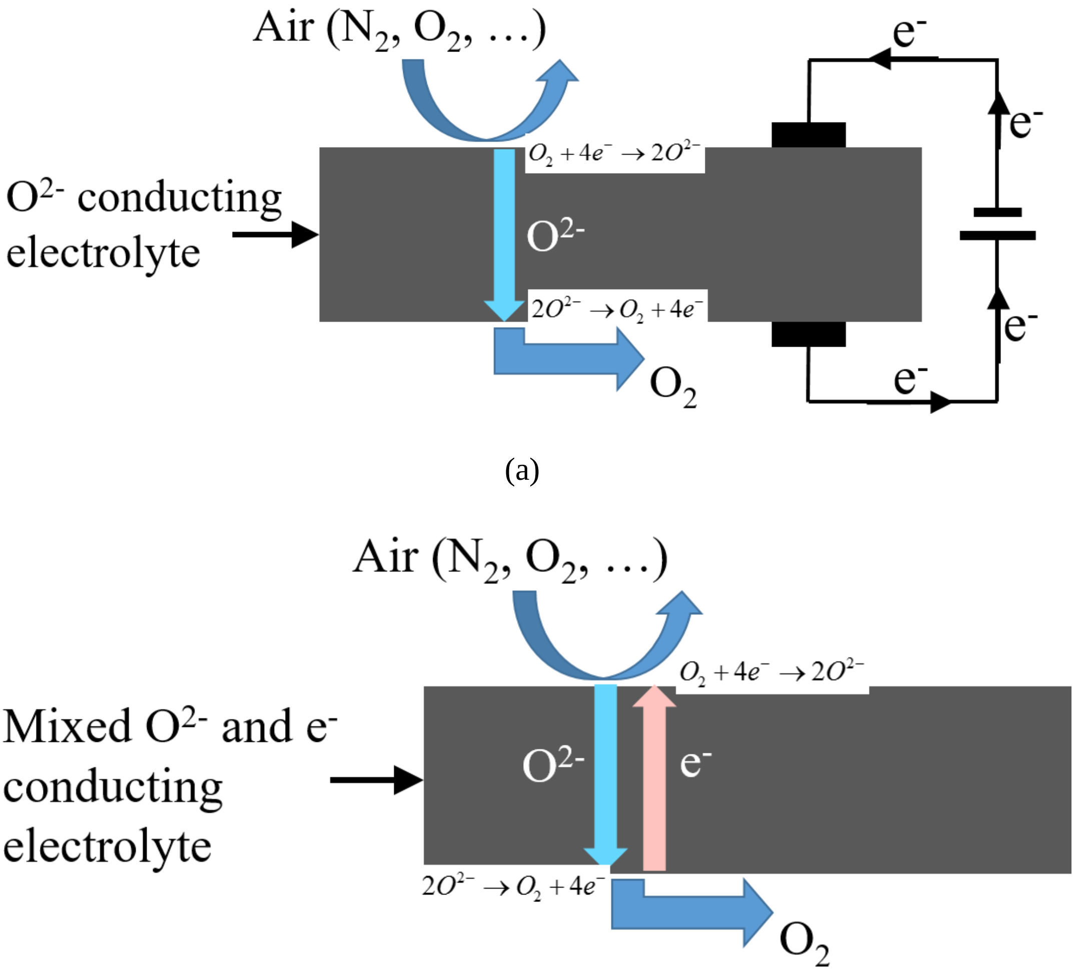

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Figure 4. Oxygen separation membrane: (a) pure ionic conducting membrane; (b) mixed ionic and electronic conducting membrane

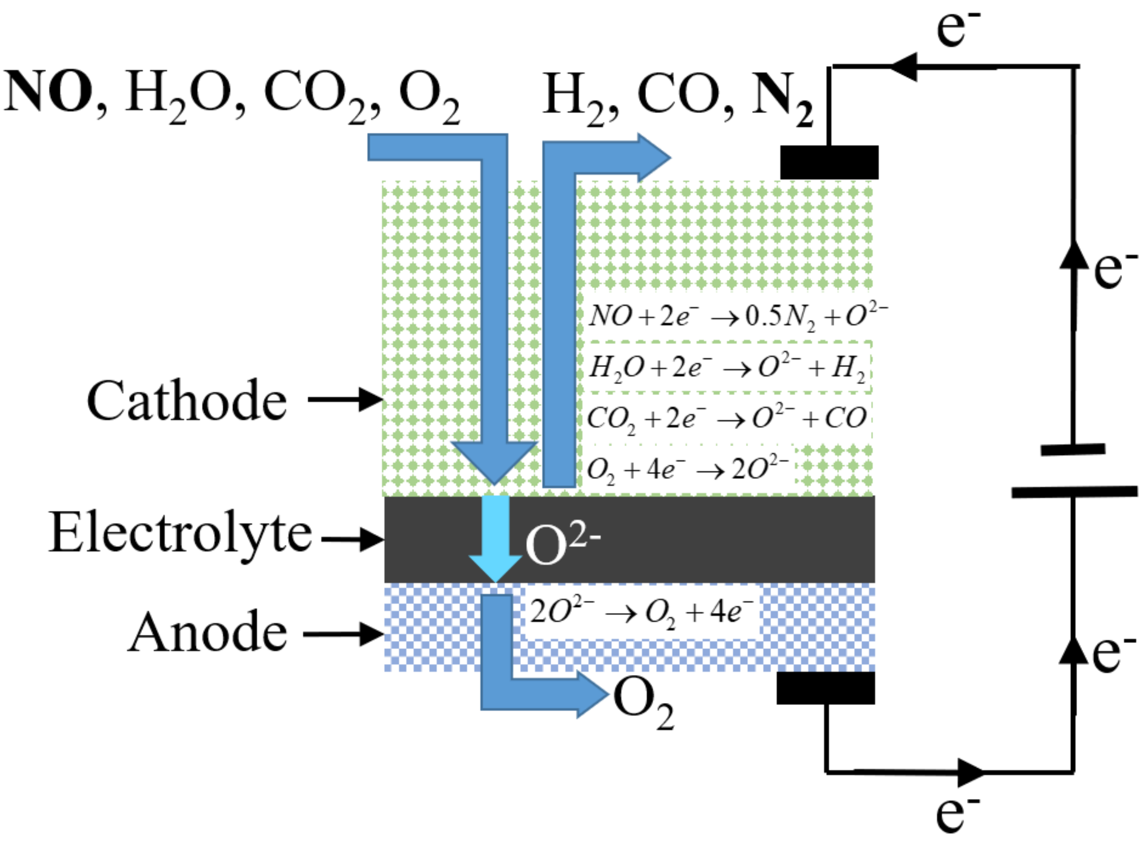
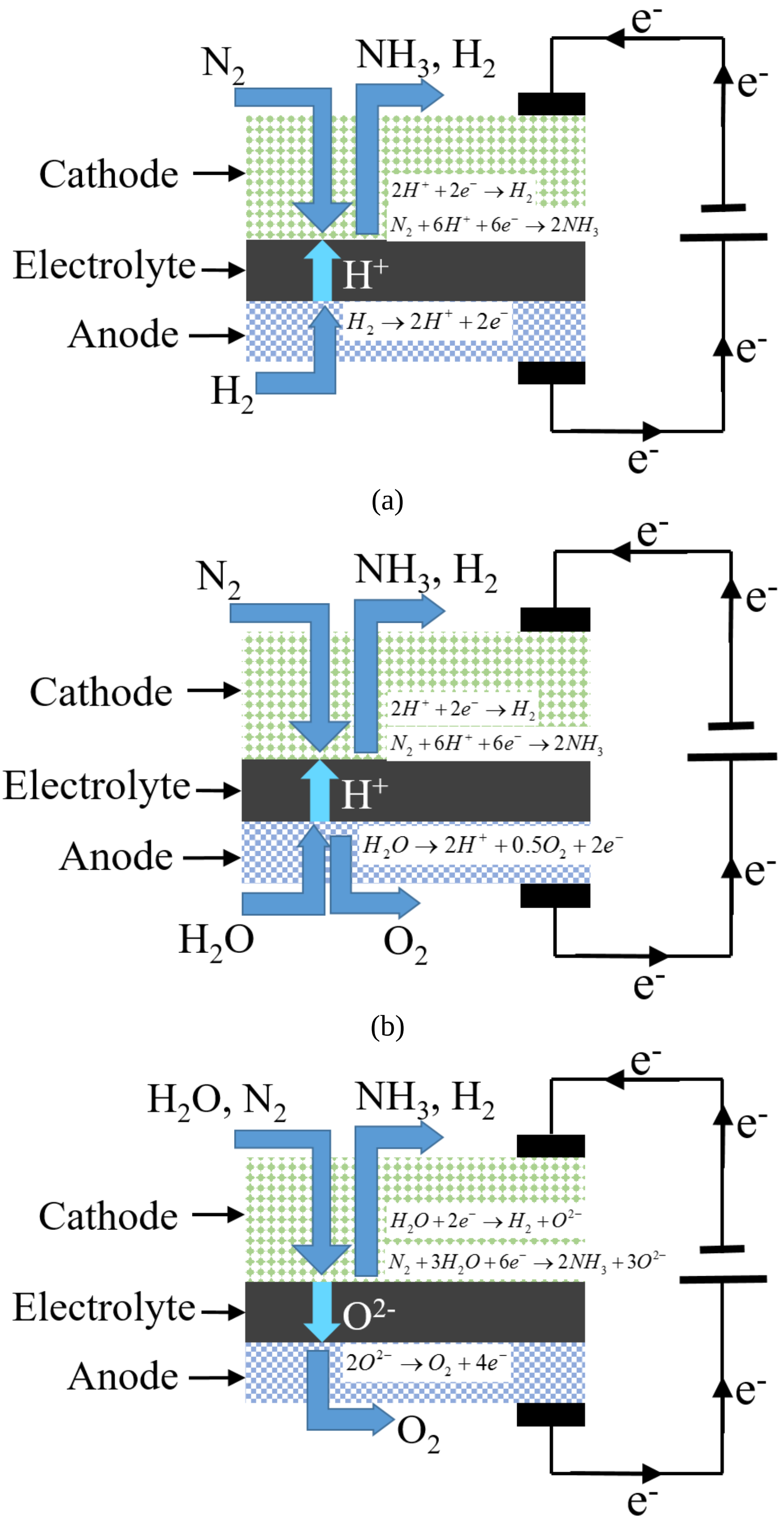


Figure 5. Solid oxide electrochemical cell for NO removal



(a)

(b)

(c)

Figure 6. Electrochemical synthesis of NH_3: (a) proton conducting electrolyte for NH_3 synthesis from N_2 and H_2; (b) proton conducting electrolyte for NH_3 synthesis from N_2 and H_2O; and (c) oxygen ion conducting electrolyte