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Progress in Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance investigations on electrochemical reactions of low temperature fuel cells operating in acidic conditions

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1. Introduction

1.1. Operating principles and properties of fuel cells

Only simple operating principles and properties of fuel cells (FCs) are explained in this section, which are essential to discuss how nuclear magnetic resonance (NMR) is used to investigate electrochemical reactions and related phenomena in low temperature FCs operating in acidic conditions as in polymer electrolyte membrane FCs and direct alcohol FCs. More detailed information on FCs can be obtained from the published reviews [1–6]. FCs are energy conversion devices which electrochemically convert chemical energies stored in fuels to produce electricity and are classified by their operating temperature, fuel type, electrolyte type, etc. [2] as summarized in Table 1. The main constituents of a FC are the anode, electrolyte, and cathode. A gas diffusion layer is attached on a catalyst layer for an anode or cathode electrode, and then an end plate (or bipolar plate for FC stacks) as shown with a schematic diagram of a single polymer electrolyte membrane FC in Fig. 1. End plates include current collectors and the flow fields for fuels or oxidants flowing through (Fig. 1). A fuel such as hydrogen passes through the flow field at the anode side while oxygen is supplied through the flow fields at the cathode side. In FCs with a proton conducting electrolyte, fuel is oxidized on anode catalysts and the protons produced from the oxidation reaction travel to the cathode and react with oxygen on cathode catalysts to produce water. In contrast, in alkaline FCs, hydroxyl ions produced at cathodes during oxygen reduction travel through alkaline electrolytes to anodes to be used for fuel oxidation at anodes. Electrochemical reactions at anode and cathode electrodes for each FC type are summarized in Table 1.

FCs are different from batteries in that the former use the chemical energy of fuel while chemical change of electrodes takes place for energy conversion in batteries. Another difference is that FCs need inlets and outlets for fuel, oxygen, and exhausts while batteries are closed systems in terms of materials. Chemical energy stored in hydrogen and several hydrocarbon fuels is significantly higher than that found in battery materials. FCs produce less pollution and noise per generated unit of electric power since they are more efficient than combustion engines or thermal process. However, to be fully commercialized, several weak points of FCs should be improved. Fuel crossover from anode to cathode should be suppressed to avoid fuel depletion without proper usage at the anode, fuel oxidation at the cathode, and a consequent reduction of electrical potential of FCs. The water content and distribution in FCs should be optimized to avoid flooding and to maintain a good conductivity at the same time. Flooding hinders the catalytic reaction of gas molecules by covering the catalytic active sites with water. However, a low water content reduces the proton conductivity of electrolytes, resulting in low current densities. Hydrogen which is a representative fuel for FCs, needs to be supplied safely and economically. The cost of FC components such as catalysts and polymer electrolyte membranes needs to be reduced. The durability and reproducibility of FCs also have room for improvement. To overcome these disadvantages, it is essential to understand the chemical reactions taking place, the distribution of chemicals, the properties of the components, and the aging and/or degradation processes of FCs.

1.2. Advantages of using NMR for studying fuel cells

NMR spectroscopy is one of the informative analytical methods [7,8] contributing to improving the performance of FCs through understanding various chemical phenomena occurring in FCs [8,9], because of the inherent characteristics of NMR spectroscopy [10–12]. The ability of NMR spectroscopy to identify chemicals can be used to monitor chemical changes occurring during the electrochemical reactions and degradation processes. NMR spectroscopy is a quantitative technique because, in general, signal intensities

Table 1
Major fuel cell types and corresponding operating temperature, electrochemical reactions, and charge carriers in the electrolytes [2].

Type	Classification	Operating temperature (°C)	Anode reaction	Cathode reaction	Charge carrier in electrolyte
PEMFC (polymer electrolyte membrane fuel cell)	Low temp. fuel cells	60–120 ∼80[a]	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2O$	H^+
DMFC (direct methanol fuel cell)	Low temp. fuel cells	60–120 ∼80[a]	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$3/2 O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	H^+
DEFC (direct ethanol fuel cell)	Low temp. fuel cells	60–120 ∼80[a]	$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$	$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$	H^+
AFC (alkaline fuel cell)	Low temp. fuel cells Middle temp. fuel cells	<100 23–70[a] 100–250[a]	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$1/2 O_2 + H_2O + 2e^- \rightarrow 2OH^-$	OH^-
PAFC (phosphoric acid fuel cell)	Middle temp. fuel cells	160–220	$H_2 \rightarrow 2H^+ + 2e^-$	$1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2O$	H^+
MCFC (molten carbonate fuel cell)	High temp. fuel cells	600–800 ∼650[a]	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$1/2 O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	CO_3^{2-}
SOFC (solid oxide fuel cell)	High temp. fuel cells	800–1000 (500–600 possible)	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$1/2 O_2 + 2e^- \rightarrow O^{2-}$	O^{2-}

[a] From Website of US Department of energy: http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc_types.html.