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Abstract

Developing in operando diagnostic techniques based on spectroscopic methods for fuel cells is vital for understanding electrochemical processes at the molecular level. In a conventional electrolytic cell, online electrochemical mass spectrometry (OEMS) can detect in real time gaseous and volatile species from solution during electrochemical reactions through a hydrophobic porous film covering the mass-spectrometer inlet. However, OEMS has not been used to detect fuel-cell catalyst layers mainly because of the large size of the sampling inlet and the method's poor ability to analyze low-volatility species. Herein, we developed a liquid-inlet OEMS method based on liquid sampling and vaporization that can effectively detect low-volatility species from solution. The sampling capillary was small and can be inserted into a fuel-cell catalyst layer to detect products and reactants effectively. This method was then used in the *in operando* monitoring of concentration variations of the reactant ethanol and the products acetaldehyde and acetic acid in a direct ethanol fuel cell.

Keywords: Online electrochemical mass spectrometry; direct ethanol fuel cell; *in operando* method; ethanol electrooxidation; electrocatalysis



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