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Improved methods to measure hydrogen crossover current in proton exchange membrane fuel cell

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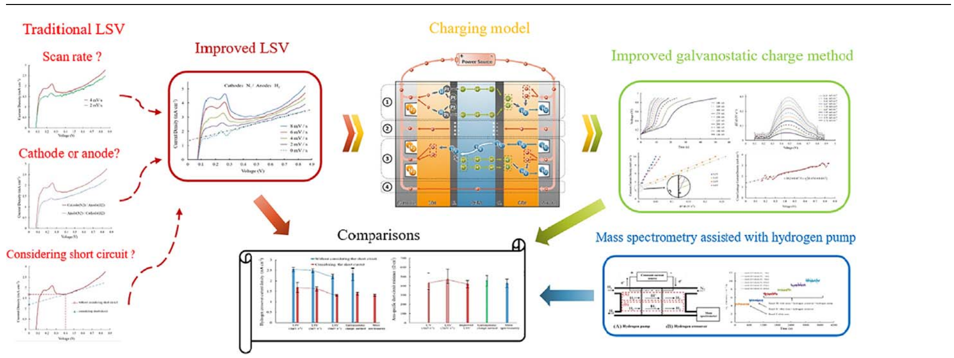
HIGHLIGHTS

- LSV is improved to eliminate negative effect of scan rate on measurement accuracy.
- Cross leakage current covers hydrogen crossover current and short-circuit current.
- A charging model of PEMFC is proposed to distinguish four electrochemical processes.
- Short-circuit resistance can be measured by improved galvanostatic charge method.
- A new mass spectrometry assisted with hydrogen pump is proposed to detect the MEA.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen crossover current has a great influence on the performance and durability of proton exchange membrane (PEM) fuel cells. The common measuring method is linear sweep voltammetry (LSV). But some usual approximations, such as ignoring the influence of scan rates or short-circuit resistances, can lead to greater measurement deviations. Therefore, in this study to accurately measure hydrogen crossover current, LSV is improved by building a novel charging model based on fitted zero scan rate curves and on taking effects of short circuit into consideration. On the basis of this new model, galvanostatic charging method is improved by taking short circuit of PEMs into consideration and a mass spectrometry assisted with hydrogen pump is proposed with no need of calibration with standard gas. Hydrogen crossover current and short-circuit resistance of a 34 cm^2 single cell are measured by three improved methods, which are then compared with methods previously available. It is found that hydrogen crossover currents are reduced and more accurate than those obtained by previous methods, and values obtained by different improved methods are highly consistent with each other. So the proposed charging model is valid and can be used to optimize other electrochemical measurements of fuel cells.

1. Introduction

Proton exchange membrane (PEM) fuel cells have attracted widespread attention as one of the future alternative energy conversion devices offering a non-pollution, high-efficiency and low-temperature power source for both stationary and portable applications, particularly for future transportation applications [1]. In order to put PEM fuel cells to large-scale industrial application, many studies have been made in

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Nomenclature

Symbols

α	charge transfer coefficient
η	overpotential (V)
ASR	area-specific resistance ($\Omega\cdot cm^2$)
C	capacitance (F)
F	Faraday's constant (96,485 $C\cdot mol^{-1}$)
I	current (A)
i	current density ($mA\cdot cm^{-2}$)
J	flow ($mol\cdot s^{-1}$)
k	ratio of effective signal to hydrogen flow rate ($C\cdot mol^{-1}$)
n	number of exchanged electrons in the reaction (2)
Q	quantity of charge (C)
R	resistance (Ω)
RH	relative humidity (%)
R_g	gas constant (8.314 $J\cdot mol^{-1}\cdot K^{-1}$)
r	cell-specific resistance ($\Omega\cdot cm^2$)
S	signals of hydrogen ion (A)
T	temperature (K)
t	charging time (s)
U	voltage between electrodes (V)

Subscripts

0	exchange
a	anode
c	cathode
cc	charging
con	contact between elements
cross	cross leakage
dl	double layer
ext	external circuit
H_2	hydrogen crossover
HP	hydrogen pump
i	ionic conduction in PEM
L	limiting
LSV	linear sweep voltammetry
noise	white noise
Ox	oxidation reaction
Pt- H	hydrogen desorption
Red	reduction reaction
sc	short circuit

many aspects, including performance [2], life prediction [3], water [4] and thermal management [5], and development of advanced PEMs [6], electrocatalysts [7] and bipolar plates [8]. The primary functions of PEM, which work as the central part of a fuel cell, are the transference of protons from anode to cathode and the formation of a barrier to prevent permeation of reactants between anode and cathode. At present, PEM can be made increasingly thinner to reduce the ionic resistance, to optimize water management and to promote the performance of a fuel cell. Nevertheless, the permeation of a certain amount of reactants is inevitable based on PEM's thickness and quality, which is called 'hydrogen crossover'.

In PEM fuel cells hydrogen crossover is usually characterized by hydrogen crossover current, which is a good indicator of the aging degree of PEM, or whether it has been perforated, and how it impacts the performance, efficiency and durability of fuel cells. In the commonly used fuel cell power generation model [9], the polarization η of a fuel cell is obtained by

$$\eta = \frac{R_g T}{\alpha_{Ox,a} F}\ln\frac{i_{ext}+i_{cross}}{i_{0,a}} + \frac{R_g T}{\alpha_{Red,c} F}\ln\frac{i_{ext}+i_{cross}}{i_{0,c}} + r_i\left(i_{ext}+i_{cross}\right) + \left(r_{ext}+r_{con}\right)i_{ext} - \frac{R_g T}{nF}\ln\left(1-\frac{i_{ext}+i_{cross}}{i_{L,a}}\right) - \frac{R_g T}{nF}\ln\left(1-\frac{i_{ext}+i_{cross}}{i_{L,c}}\right) \quad (1)$$

where i_{cross} is the cross leakage current density ($mA\cdot cm^{-2}$), whose value is mainly determined by the state of a PEM and approximately equal to hydrogen crossover current density. It can be discovered from Eq. (1) that hydrogen crossover current density is positively related with overpotential η, the increase of which leads to performance degradation of a fuel cell [10]. Furthermore, hydrogen crossover can also attributable to poor membrane and lead to further deterioration of membrane electrode assembly (MEA), particularly the membrane itself [11] and cathode catalyst layer materials [12]. In short, hydrogen crossover accelerates the aging of MEA and reduces the lifetime of fuel cells. In this

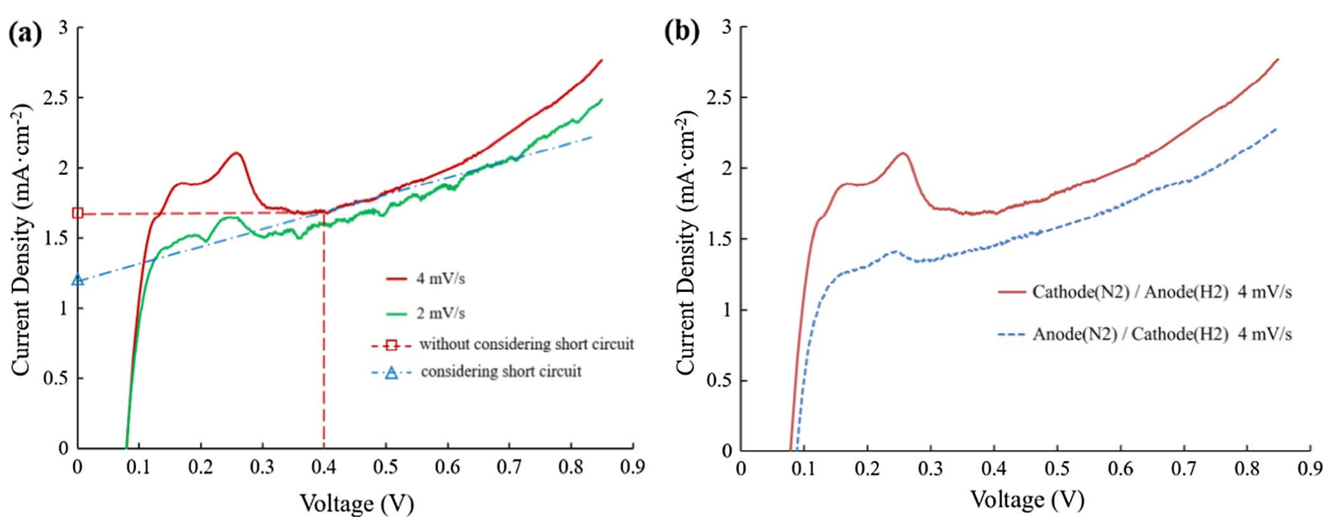

Fig. 1. Measurements of hydrogen crossover current by traditional LSV: (a) measurements at different scan rates; (b) measurements in different charging directions.