Journal of Magnetic Resonance 269 (2016) 157–161

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Communication

3D printed sample holder for in-operando EPR spectroscopy on high temperature polymer electrolyte fuel cells

Arvid Niemöller [a], Peter Jakes [a,*], Steffen Kayser [a], Yu Lin [b], Werner Lehnert [b,c], Josef Granwehr [a,d]

[a] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-9), 52425 Jülich, Germany
[b] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-3), 52425 Jülich, Germany
[c] Faculty of Mechanical Engineering, RWTH Aachen University, 52072 Aachen, Germany
[d] Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, 52056 Aachen, Germany

ARTICLE INFO

Article history:
Received 22 February 2016
Revised 10 May 2016
Accepted 4 June 2016
Available online 6 June 2016

Keywords:
EPR spectroscopy
3D printing
In-operando
High temperature PEM fuel cell
HT-PEFC
Sample holder

ABSTRACT

Electrochemical cells contain electrically conductive components, which causes various problems if such a cell is analyzed during operation in an EPR resonator. The optimum cell design strongly depends on the application and it is necessary to make certain compromises that need to be individually arranged. Rapid prototyping presents a straightforward option to implement a variable cell design that can be easily adapted to changing requirements. In this communication, it is demonstrated that sample containers produced by 3D printing are suitable for EPR applications, with a particular emphasis on electrochemical applications. The housing of a high temperature polymer electrolyte fuel cell (HT-PEFC) with a phosphoric acid doped polybenzimidazole membrane was prepared from polycarbonate by 3D printing. Using a custom glass Dewar, this fuel cell could be operated at temperatures up to 140 °C in a standard EPR cavity. The carbon-based gas diffusion layer showed an EPR signal with a characteristic Dysonian line shape, whose evolution could be monitored in-operando in a non-invasive manner.

1. Introduction

Spectroscopic ex-situ and in-situ measurements are widespread to study electrochemical systems such as batteries, fuel cells and electrocatalytic converters [1–3]. Such analyses imply an interruption of the chemical and physical processes while the measurements are performed. In-operando methods, where spectroscopic experiments and electrochemical cell operation are conducted simultaneously, offer the chance to get a deeper understanding of the mechanisms and issues related to the materials and devices. Real running conditions can be applied while the system is analyzed by a non-destructive and ideally also non-invasive analytical method. However, to be compatible with a particular spectroscopic modality, dedicated cells must usually be developed [4,5]. For magnetic resonance, electrically conductive materials and components inside a resonator reduce its quality factor and the skin effect causes shielding of parts of a cell. Nonetheless, different designs have been shown to provide good results both for in-operando nuclear magnetic resonance (NMR) [6–9] and for electron paramagnetic resonance (EPR) [4]. For example, in-operando EPR of electrochemical cells has been performed for Nafion® based fuel cells [5], for lithium batteries [4,10] or for catalytic systems [11]. A set of specifications can be summarized for this purpose: The cell has to fit into the EPR resonator that offers limited space, the sample holder should not show an EPR signal that disturbs the measurement or complicates its analysis, and the sample holder must enable the functioning of the electrochemical system. In addition, the sample holder material should not decrease the quality factor of the resonator. Thus, for each experiment an individual cell design was developed to meet the requirements for EPR detection, a process that is complicated and requires high precision during the construction and assembly stage.

Electrochemical cells generally consist of a stack of materials that can be divided into two half cells, the anode and the cathode. For EPR spectroscopy, such cells are challenging for several reasons [4,5,12]. Although electrochemically inactive, electrically conductive current collectors are necessary for contacting the cell. Since conductive materials are shielding electromagnetic radiation, the volume of interest does not get excited homogeneously. In particular, a Faraday caging effect has to be avoided and eddy currents must be minimized. The current collector is connected to the electrochemically active electrode, which is usually the material of interest. It must be ionically conductive and also exhibit some electrical conductivity. The electrical conductivity could change during cell operation, for example as a function of the state of charge of a

* Corresponding author.
E-mail address: p.jakes@fz-juelich.de (P. Jakes).

http://dx.doi.org/10.1016/j.jmr.2016.06.003
1090-7807/

battery or of the current at which a fuel cell is run. This can change the mode of an EPR resonator during the course of an experiment, leading to systematic errors when quantifying the number of spins contributing to the spectrum, to a shift of the EPR resonances or to a phase shift of the signal. Both half cells are separated by an electrically insulating, but ionically conductive electrolyte. It can be doped to enhance ionic conductivity, which could complicate the EPR spectrum due to additional signal components. In general, each electrochemical cell setup requires its own compromises. No optimal design exists, hence a tool for quickly testing the suitability of different design choices would be particularly desirable.

Polymer electrolyte fuel cells (PEFC) are classified according to their operation temperature as low temperature (LT) PEFC and high temperature (HT) PEFC. Low temperature is defined as the region below 100 °C, high temperature covers a range from 100 °C to 200 °C. Nafion® based membranes of LT-PEFCs have to be kept fully hydrated to ensure high proton conductivity [13]. For HT-PEFCs with a typical operating temperature of 160 °C and, e.g., a phosphoric acid doped polybenzimidazole (PBI) membrane, condensation is not relevant because water is in the vapor phase. This high operating temperature results in enhanced electrode kinetics, but the adsorption of phosphoric acid on the Pt catalysts, which is temperature, concentration and potential dependent, is still an issue that needs to be solved [14,15]. The main advantages of a HT-PEFC are the high CO-Tolerance up to 1–5 vol% [16–18] and the fact that no external humidification of the gases to prevent drying out of the membrane is necessary [19,20]. Moreover, the cooling system can be designed more compactly due to the high temperature difference between stack temperature and ambient temperature [21,22]. Furthermore, the surplus energy at high temperatures can be used efficiently in a system [23]. To investigate PEFCs, spectroscopic techniques have proved particularly successful [24–26]. However, despite intensive research, proton transport mechanisms in HT-PEFCs and LT-PEFCs are still not fully understood [27–34].

While EPR spectroscopy was demonstrated for LT-PEFCs to provide useful information of chemical processes inside the cell [5,35–37], the implementation and construction of HT-PEFCs for in-operando EPR presents additional challenges. The EPR cavity has to be protected against the operation temperature in the range from 100 °C to 200 °C, whereas the fuel cell has to be heated since the heat produced during reaction is too small for maintaining the necessary temperature.

A new technique for flexible custom component and device production is 3D printing, which developed at an incredible pace in the last few years [38] and can be well utilized for EPR spectroscopy. In contrast to conventional manufacturing processes, constructions can be printed directly with gaps and holes. The post processing after printing is short and not very costly. In general, this modality presents a rewarding alternative to produce parts rapidly, cheaply and from a range of different materials.

In this communication, the design of a HT-PEFC for in-operando EPR at X-band in a commercial resonator is described. By manufacturing the cell housing using a 3D printer, it is demonstrated that this modality is suitable to produce containers for complicated EPR samples. The usability of different 3D printing materials for EPR experiments is investigated. The performance of the setup is shown and the potential of in-operando EPR for HT-PEFCs is discussed.

2. Fuel cell design suitable for in-operando EPR

Protection of the EPR resonator is essential for high temperature applications, because standard commercial cavities are designed for maximum permanent temperatures of about 60 °C. A temperature in the range of 100–200 °C would destroy the resonator during long term experiments. Therefore, the fuel cell dimensions were specified to fit into a Dewar vessel made of quartz glass with an outer diameter of 10 mm and an inner diameter of 7 mm, which was placed inside the EPR resonator. The inside of the Dewar vessel can be heated from the bottom with hot nitrogen gas. With this setup, samples with a diameter of up to 7 mm can be heated to approximately 400 °C using a standard EPR cavity. During cell operation at 140 °C, no significant temperature increase of the EPR resonator was noticed.

The housing material for HT-PEFCs needs to withstand an operation temperature of at least 100 °C and should be EPR silent. To test the suitability of 3D printing for fuel cell housing production, different 3D printing materials were analyzed with respect to EPR signal and heat resistance. Four materials were tested: a high temperature polymer (OBJET RGD525, Stratasys), ABS (Terluran GP22, BASF), Nylon-12 (Vestamid L1940, Evonik) and polycarbonate mixed with 10% glass fibers (Makrolon 9415, Bayer). EPR spectra of the four materials are shown in Fig. 1.

The high temperature polymer and Nylon-12 showed EPR signals, while ABS and polycarbonate were EPR silent. The heat resistance of polycarbonate is higher than that of ABS. It can be used up to permanent temperatures of 140 °C, which is a useful temperature limit for first HT-PEFC experiments.

The cell housing consists of two half casings to facilitate the assembly of the cell. Once assembled, the two halves were screwed together and also held in place by a snap-in mechanism. The total length of the cell is 60 mm and the maximal diameter is 6.9 mm. The design of one half of the full cell housing is shown in Fig. 2a. The cell design was exported in the STEP file format from a CAD program (Autodesk® Inventor®) and produced with a 3D printer (Fortus 400mc™) that uses a solid polycarbonate raw material supply.

The gas inlet of the half-casing is shown on the right-hand side of Fig. 2a. The gas enters the flow channel above the active areas of the cell through a feeding channel with a diameter of 1 mm. The flow channel is 10 mm long and 1.5 mm wide. The size of the channel and therefore the sample size is limited by the microwave absorption of the carbon gas diffusion layer (GDL) with microporous layer (MPL) and platinum on carbon black. A high amount of absorbing carbon in the GDL is detrimental to the EPR signal, resulting in a low S/N ratio. Hence a small sample size is most beneficial. The gas outlet is on the opposite side of the flow channel with respect to the inlet. Inside the flow channel three bars with a triangular top support the gas diffusion electrode and press it onto the membrane.

The two halfcasings are placed on top of each other with the membrane electrode assembly in between. The abovementioned snap-in mechanism helps to adjust and to maintain the correct alignment of the components. Additional holes for screws can be used to fix the half-casings tightly onto each other. The assembled fuel cell contains three layers of material each on the cathode and on the anode side. In addition, instead of the electron conducting flow field used in conventional fuel cells, a gold wire provides the electrical connection to the outside of the cell. The 100 μm thick gold wire is laid inside the gas feed channels and pressed onto the GDL for contacting. The catalyst is coated onto the carbon support and is pressed on the PBI membrane (Fig. 2b).

3. In-operando fuel cell operation

Fig. 3a shows the EPR spectrum of the inactive fuel cell, i.e. without gases flowing. It exhibits a Dysonian line shape [39], which is well known to occur for conduction electrons in graphitic carbon [40] and is a function of conductivity of the material, the