



Short communication

Interdigitated metal electrodes for high-resolution *in situ* electrochemical NMR



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ABSTRACT

Despite being among the most widely used spectroscopic methods, high-resolution NMR has not yet been applied routinely to electrochemistry and (organic) electrosynthesis, due largely to the incompatibility between NMR detection and electrical conduction of electrochemistry. Here, we introduce a straightforward, easy-to-construct system that incorporates high-resolution (HR) *in situ* NMR spectroscopy with electrochemistry by using cylindrically symmetric interdigitated metal (Au) electrodes. The constructed system is simple to build, inexpensive, and robust. It requires with minimal setup time and can be used with conventional commercial probes without the need of any modifications to them. To demonstrate the feasibility and performance of the system, we used ^1H NMR to monitor the reversible redox reaction of ferrocene and ^{13}C NMR to follow the electro-oxidation reaction of methanol on a commercial PtRu electrocatalyst.

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1. Introduction

Electrolysis and electrochemical (EC) techniques are ubiquitous in modern chemical research, and are the dominant processes in a wide variety of active research areas, including energy research (hydrogen production, batteries, and fuel cells) [1–3], organic synthesis [1,4], and large-scale industrial chemical production methods [5,6]. However, the exact pathways of many reactions employed in these electrolysis and electrochemical processes are not well-understood, preventing optimization and the maximization of utility of the reactions. Various *in situ* methods have been established to monitor electrochemical reactions with the aim to aid investigations in these fields, including Fourier transform infrared, mass spectroscopy, UV–vis, and surface enhanced Raman spectroscopy [7,8].

Nuclear magnetic resonance (NMR) is among the most powerful of spectroscopic methods, but has been much underutilized in EC studies due to technical complications [9]. In most cases, the metallic electrodes essential to electric conduction in EC experiments have an adverse effect on the sensitivity and resolution of the typical NMR probe and preclude its use. However, because of its significant potential as a spectroscopic tool with high chemical specificity and capability to non-invasively probe bulk molecules in any phase, significant effort has been made to overcome the incompatibilities that prevent the use of *in situ* NMR to monitor and study EC reactions [9–14]. The majority of these efforts, however, involve specialized techniques and/or involve

specialized construction of NMR EC cells or probe modifications. While some of these systems have demonstrated impressive feasibility, NMR has not yet found general application in EC measurements due to these and other technical limitations.

In this work, we describe an easier implementation of *in situ* EC-NMR spectroscopy. It was developed after our adaptation of Dunsch's rather simple approach [12] still revealed some remaining technical inconveniences [14]. The new system was designed to be constructed by researchers in a typical chemistry lab, with no additional training or extensive construction methods and using only common equipment. We in particular avoided any necessity of glasswork, epoxy sealing, or the need to modify the commercial NMR probes common to most user facilities, and the system does not require a dedicated NMR instrument. To ensure its utility to the widest possible community, we prioritized a system that was stable for long reaction times, had multi-nuclear capability, maintained the important high-resolution feature of solution-state NMR, and could be used for aerobic or anaerobic reactions.

2. Experimental

Typical ^1H NMR spectra were recorded using a 5 μs excitation pulse length with 100 ms repetition times and 100 averaged acquisitions. The time interval between two consecutive spectra was about 4.5 min. Ferrocene was used at 15 mM concentration with 0.1 M Bu_4NPF_6 in *D*-acetonitrile for the ^1H NMR study. During the oxidation cycle, the potential was held at +40 mV with respect to an Ag/AgCl reference. Electrochemical currents were around 50 μA . During the

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reduction cycles, the potential was held at -60 mV and currents were measured around -100 μ A.

Typical ^{13}C NMR spectra were recorded using 10 μ s excitation pulse length with 20 s repetition times and 48 averaged acquisitions. The time interval between two consecutive spectra was about one hour. The ^{13}C -labeled methanol $^{13}\text{CH}_3\text{OH}$ (99% Sigma Aldrich) was used at a concentration of 5 M with 0.01 M HClO_4 (Sigma Aldrich) in D_2O . Oxidation was achieved by holding the potential at $+600$ mV with respect to an Ag/AgCl reference. The reaction was catalyzed with activated commercial PtRu black nanoparticles drop-cast onto the WE and covered with Nafion solution.

All of the *in situ* ^{13}C and ^1H NMR spectra were acquired at 25°C using a hybrid Bruker/Tecmag 300 MHz spectrometer with a standard 5 mm multi-nuclear probe. All spectra were referenced to TMS. Potentials were applied with a Voltlab PGZ100 potentiostat, and current was monitored during the NMR experiments.

The EC-NMR system is shown schematically in Fig. 1. It uses interdigitated gold electrodes (iges) deposited on a pre-cleaned polyimide (Kapton) film, which is then inserted into a standard NMR tube of the desired diameter (5 mm, 10 mm, etc.) without the need of any glass-work and epoxy sealing. One of the electrically isolated electrodes acts as the working electrode (WE) and the other as the counter electrode (CE). Gold was used preferentially due to its chemically inert nature. A Ag/AgCl pseudo-reference electrode (RE) was also inserted into the NMR tube and maintained above the NMR sensitive detection region.

2.1. Interdigitated electrodes

The IGE system provides a simple solution to many of the issues that other EC-NMR systems have sought to solve by involved or intricate engineering means. Electrochemical optimization requires working and counter electrodes that are both large in surface area and close in physical proximity to one another. The interdigitated configuration elegantly

achieves these experimental demands by providing electrodes that not only have a large surface area, but also have that area everywhere nearby by the opposing counter electrode. The IGE configuration thus promotes good electrochemical performance.

Co-locating the counter and working electrodes within the NMR coil does have experimental tradeoffs. While it maximizes the sensitivity of the NMR experiment to the intermediate products of a reaction, those intermediates may react with each other or the initial reactants, potentially complicating analysis and interpretation. Of course, it is an easy matter to make an IGE setup with the counter electrodes shorter than the working electrodes, allowing the counter electrode strips to remain above the NMR region. Nonetheless, the common electrolyte reservoir will equalize chemical concentrations, and this shortcoming should be understood. Similarly, unwanted intermediates may be detected due to the presence of the counter electrode in the NMR coil.

Along with the electrochemical considerations, we must also consider the electrical effects of the IGE on the NMR probe. The presence of metal in the induction coil of an NMR probe normally leads to deleterious effects for one (or more) of four main reasons: susceptibility, eddy currents, detuning of the radiofrequency (RF) coil, or RF screening. A thin IGE configuration largely avoids or corrects these issues. First, the cylindrical geometry of the iges in the sample tube limit distortions caused by magnetic susceptibility to symmetric inhomogeneities that are easily corrected by shimming. Second, eddy currents are minimized by the IGE geometry; the thin electrically isolated electrodes preclude connected electrical paths around the sample. Finally, restricting the iges to a thickness much less than the RF skin depth at the Larmor frequency minimizes detuning of the RF coil and eliminates RF screening effects.

The iges provide the means to incorporate electrodes into the NMR coil without significant sensitivity loss. The thickness of the gold deposition is an important parameter in the final system performance; 40 – 50 nm thick proved optimal for our commercial probes. This thickness provided low resistivity (around 150 Ω from top to bottom) while reducing the probe quality factor (and thus sensitivity) by about only a few percent. Also important in the final sensitivity of the IGE system is the concentration of conductive acidic electrolyte. At high concentrations, the conductive electrolyte can significantly degrade the probe sensitivity; we used a concentration of 0.01 M HClO_4 which reduced the probe sensitivity by about 18% . The skin depth of gold at our frequencies is <5 μm ; keeping the thickness of the electrodes to one percent of this value in a cylindrically

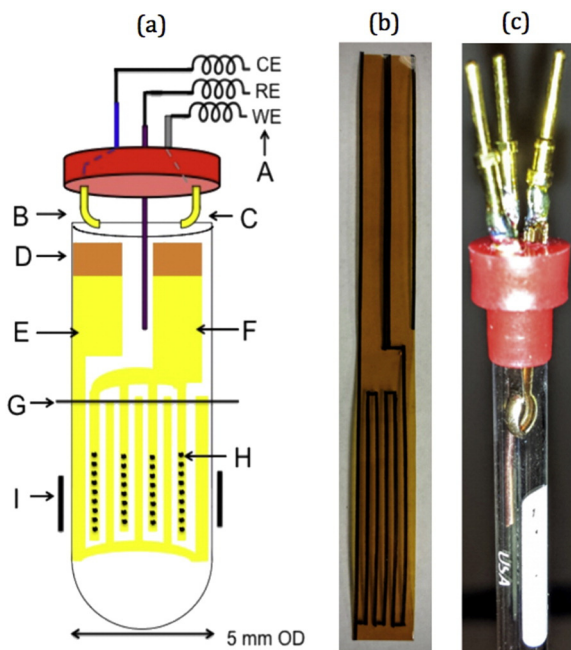


Fig. 1. a) Schematic of the IGE EC-NMR system setup. The system can be incorporated into a 5 -mm commercial NMR tube and thus used in standard high-resolution solution NMR probes. The components are: A— 200 μ h inductors as RF chokes, B—CE electrical finger, C—WE electrical finger, D—Cu tape, E—CE interdigitated electrode, F—WE interdigitated electrode, G—electrolyte level in NMR tube, H—catalyst, and I—NMR coil. (b) The polyimide (Kapton) strip shown before the mask is removed to reveal the interdigitated gold electrodes. (c) The NMR cap in place on an empty NMR tube. The electrodes in (b) will be rolled lengthwise into a cylinder and inserted into the NMR tube for an experiment.

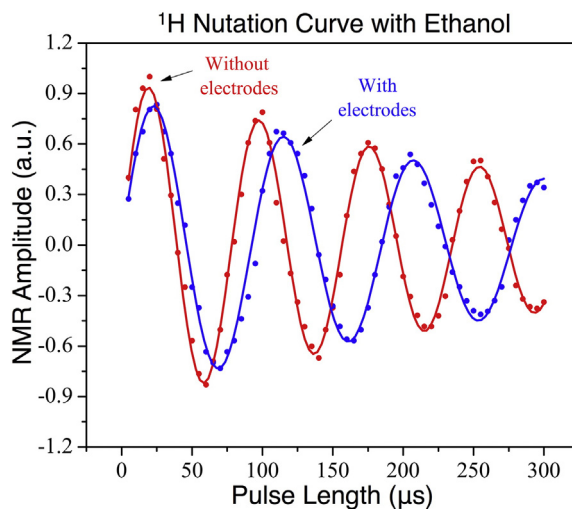


Fig. 2. ^{13}C NMR nutation curve with and without the iges present. The pulse lengths remain approximately the same up to the 90 degree pulse, but get longer for large tip angles due to rf absorption by the metal electrodes. The amplitude reduction is due to decreased sensitivity and sample exclusion from the NMR coil.

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