Construction of ^{19}F-^{13}C Solid-State NMR Probe for 400MHz Wide-Bore Magnet

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Abstract   Various fluorine-containing materials are used in electronic devices like LCD display panels and Li-ion batteries. The structural conformation of fluorine in fluorinated materials is an important contributing factor that influences the chemical and physical properties. The conformation can be changed by heat and stress during manufacture or use. Understanding the conformational changes is critical for understanding the performance and durability of electronic devices. Solid-state NMR spectroscopy could be widely used for the analysis of various fluorine-containing materials for electronic devices. However, conventional CPMAS probes cannot be used for in-situ analysis of fluorine-containing electronic devices like LCD panels and Li-ion batteries. In this paper, we show the design, construction, and optimization of a ^{19}F-^{13}C double-resonance solid-state NMR probe for a 400MHz wide-bore magnet with a flat square coil for in-situ analysis of fluorine-containing electronic devices without observing fluorine background signals. This custom-built probe does not show any fluorine background signals, and can have higher efficiency for lossy samples.

Key Words: Solid-state NMR probe, Home-built, Fluorine background signal, In situ analysis

Introduction

The various fluorinated materials have been used widely in domestic appliances, automobiles, and high-tech devices like LCDs and Li ion batteries. The physical, electrical, and optical properties of these materials change according to the synthetic strategies used, because the structural conformations and microstructures could be changed. In some cases, a considerable change for these properties is caused by just a small difference in the conformation.[1-3] Thus, it is important to know how changes in conformation affect the physical and chemical properties. Nuclear magnetic resonance (NMR) spectroscopy has been widely used for the analysis of fluorinated materials, with which most materials are analyzed in solution.[4,5] However, this method is limited for the analysis of conformation and structures of fluorinated polymers, because of the limited solubility for solvents. The analysis of conformation in solution is uninformative for obtaining the exact conformation.[6,7] This problem could be solved by magic angle spinning (MAS) in solid-state NMR spectroscopy, which can be used to investigate the relationships between the conformation and physical properties.[8,9] However, MAS solid-state NMR spectroscopy is not sufficient for structural studies in some cases such as in-situ device analysis.

Electronic devices such as LCD panels and Li-ion

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batteries contain various fluorinated materials, and the conformational changes of these materials could occur during use or manufacture, which affects the performance and durability. These conformational changes are closely related to the development of electronic devices. In order to study these conformational changes of a device, a specialized solid-state NMR probe is needed.

In this paper, we present the design, construction, and optimization of a ^{19}F-^{13}C double-resonance solid-state NMR probe with a flat square coil for a 400MHz wide-bore magnet without a fluorine background signal. It could be applied to the in-situ analysis of electronic devices like LCD panels and Li ion batteries without a fluorine background signal.

Experimental Methods

Probe Design and Construction- The custom-built solid-state NMR probe heads with ^{19}F-^{13}C double-resonance for 400MHz wide-bore (WB) magnet parts were designed as described before. [10] However, two versions of custom-built solid-state NMR probe heads with a variable capacitor made of polytetrafluoroethylene (PTFE) (FC400A) and a variable capacitor made of quartz (FC400B) were constructed, as shown in Figure 1.

A radio frequency coil with 5 turns for the FC400A and one with 4 turns for the FC400B were used with a flat square coil, which has dimensions of 12 mm x 14 mm x 2 mm. A $\lambda/4$ coaxial cable composed of silver-coated copper, an insulator, and copper shield was used to help with ^{19}F nuclei tuning. A $\lambda/4$ coaxial cable with PTFE insulator was used in the FC400A probe, and a $\lambda/4$ coaxial cable with an air insulator with a polyethylene (PE) supporter was used in the FC400B probe, as shown in Figure 2.

Probe Circuits- The optimized and finalized probe circuit is represented in figure 3. [11] The FC400A and FC400B custom-built solid-state NMR probes were tuned to observe the ^{19}F and ^{13}C nuclei, and the impedances of all probe circuits were matched to 50 by a network analyzer (Hewlett Packard 85046A,
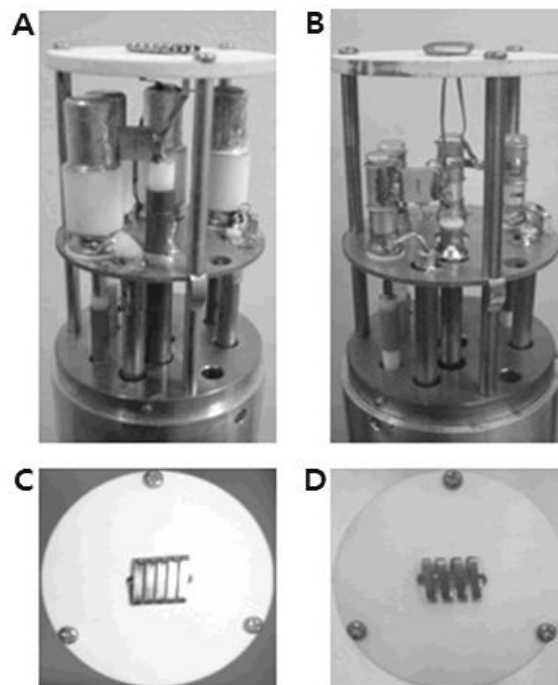
USA) outside the magnet.

Figure 1. The custom-built solid-state NMR probe heads with ^{19}F-^{13}C double-resonance for 400MHz wide-bore (WB) magnet parts. Two probe head versions were constructed, with (a) a variable capacitor made of PTFE (FC400A) and (b) a variable capacitor made of quartz (FC400B). A radio frequency coil for (c) FC400A with 5 turns and (d) FC400B with 4 turns were used with a flat square coil.
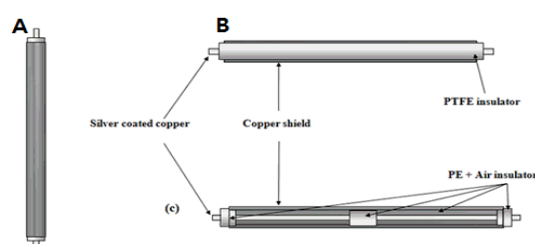

Figure 2. The $\lambda/4$ coaxial cable (a) to help with ^{19}F nuclei tuning is composed of silver-coated copper, an insulator, and copper shield. The $\lambda/4$ coaxial cable with PTFE insulator was used in (a) the FC400A probe, and the $\lambda/4$ coaxial cable with an air insulator with PE supporter was used in (b) the FC400B probe.

The ^{19}F channel was tuned and matched with the $\lambda/4$ line and the C3, C4, and C5 capacitors. The ^{13}C channel was tuned and matched with the C1, C2, and

C6 capacitors. The C7 capacitor and a short impedance coil were used to minimize the high-frequency interference of ^{19}F in the low-frequency ^{13}C channel. Capacitors C5 (8.2 pF), C6 (10 pF), and C7 (27 pF) are fixed capacitors (American Technical Ceramics, USA), and capacitors C1, C2, C3, and C4 (0.8-10 pF, 2.5-kV RF capacity) are variable capacitors made by quartz in the FC400B probe.
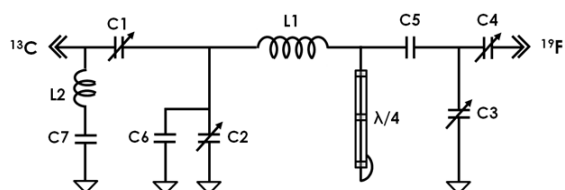

Figure 3. The schematic circuit diagram of custom-built 400MHz flat square coil [19]F-^{13}C double-resonance wide-bore probe (FC400B). Each channel ([19]F = 376 MHz and [13]C = 100 MHz) was tuned and matched by fixed and variable capacitors and λ/4 coaxial cable. Capacitors C5 (8.2 pF), C6 (10 pF), and C7 (27 pF) are fixed capacitors (American Technical Ceramics, USA), and capacitors C1, C2, C3, and C4 (0.8-10 pF, 2.5 kV RF capacity, Johanson, USA) . L1 is a flat square coil made of copper plate wire.

The variable capacitors made of PTFE were initially used to as variable capacitors in the FC400A probe, but they were changed to variable capacitors made of quartz without a fluorine component to remove the ^{19}F background signal in the FC400B probe. The coaxial cable with the PTFE inner insulator was also changed to a coaxial cable with an air insulator and PE supporter as a λ/4 coaxial cable to filter the ^{19}F frequency to eliminate the background signal in the FC400B probe.[12] The PE supporter was used to prevent contact between the inner copper core and outer copper shield. The length of the λ/4 coaxial line for the ^{19}F resonance frequency was calculated using the shortening factors of air and PE:

$$\text{Length of } \lambda/4 \text{ line} = \frac{c \cdot k}{4 \cdot v} =$$

$$\frac{3.00 \times 10^{10} (\text{cm/sec}) \times 0.702}{4 \times 376.19 \times 10^6 (\text{Hz})} \doteqdot 14.0 \text{ cm}$$

where c is the speed of light, k is the shortening factor of the insulator (air and PE supporter), and v is

the resonance frequency of fluorine in a 9.4-Tesla magnet (v_0= 376.19 MHz). The initial length of the λ/4 line was calculated as the average value (0.83) of the shortening factors for air (1) and PE (0.667), and then the length was optimized by tuning and matching using the ^{19}F frequency and a network analyzer. The shortening factor of air and the PE supporter was back-calculated from the optimized length by trial and error. The finalized length of the λ/4 line and shortening factor for the air inner insulator and PE supporter were 14.0 cm and 0.702, respectively. All parts for the probe head, including the probe body, coil mounting plate, fixed capacitors, variable capacitors, etc., were made with aluminum, brass, ceramic, quartz, and PE, which that have no fluorinated materials.

NMR Experiments- TFE (2,2,2-trifluoromethanol, ACROS Organics, Belgium) in a capillary wrapped with a PE bag was used as an external ^{19}F chemical shift standard (δ = 77.03 ppm). The single excitation pulse sequence was used without a sample tube in the receiver coil of the probe. All spectra for a commercial 4-mm T3 HXY CPMAS probe (Agilent, USA) and the FC400A and FC400B custom-built probes were acquired in a unity *INOVA* NMR spectrometer (Agilent, USA) with a 9.4-Tesla 89-mm wide-bore Oxford superconducting magnet (OXFORD instruments, UK).

Results

The ^{19}F spectrum obtained using the commercial T3 HXY CPMAS probe head showed a broad ^{19}F background signal, as shown in figure 4a. The half width at maximum height was about 40 kHz. This ^{19}F background signal can adversely affect the interpretation of the NMR spectrum, because the signal of sample was buried by the high intensity of the background signal. The initial design of the CF400A probe was aimed to remove the fluorine source in the receiver coil

chamber, as shown in figures 1a and 1c. The receiver coil plate was made of ceramic materials that have no fluorinated materials instead of PTFE. However, the broad background signal was overlapped with the sharp signal of TFE at about -77ppm in the ^{19}F NMR spectrum obtained with a sample of tri-fluoroethanol (TFE) using the FC400A probe, as shown in figure 4b. The signal of TFE could not be distinguished from the huge background signal. Therefore, the variable capacitors containing PTFE in the CF400A probe were changed to variable capacitors containing quartz in the CF400B probe, as shown in figure 1a and figure 1b. The insulator of the λ/4 transmitting line was also changed from a PTFE insulator to air and PE, as shown in figure 2. The broad background signal obtained using the CF400B probe disappeared, and a sharp signal of TFE at -77.03 ppm was obtained with a high S/N ratio that was sufficient to observe the fluorinated material, as shown in figure 4c. The finalized schematic circuit diagram of the custom-built ^{19}F-^{13}C double-resonance probe with a flat square coil for a 400MHz wide-bore magnet is shown in figure 3. Two channels for ^{19}F (ω_o= 376 MHz) and ^{13}C (ω_o= 100 MHz) were tuned and matched well by fixed capacitors (C5, C6, and C7), variable capacitors (C1, C2, C3, and C4), and λ/4 coaxial cable. The flat square coil was made of copper plate wire. The FC400B probe was optimized for a lossy sample, like with fluorinated materials in electronic devices. These samples need a high-power RF pulse excitation in solid-state NMR experiments, since heavy loss of the excitation pulse power occurs with such samples. The loss generated from the heating of the receiver coil and the sample and RF heating can deteriorate the sensitivity and resolution of NMR signals, or cause damage to the receiver coil.[13-15] The flat copper strap used in in this experiment has an advantage, because it has a relatively higher heat capacity and RF pulse efficiency than thin copper wire.
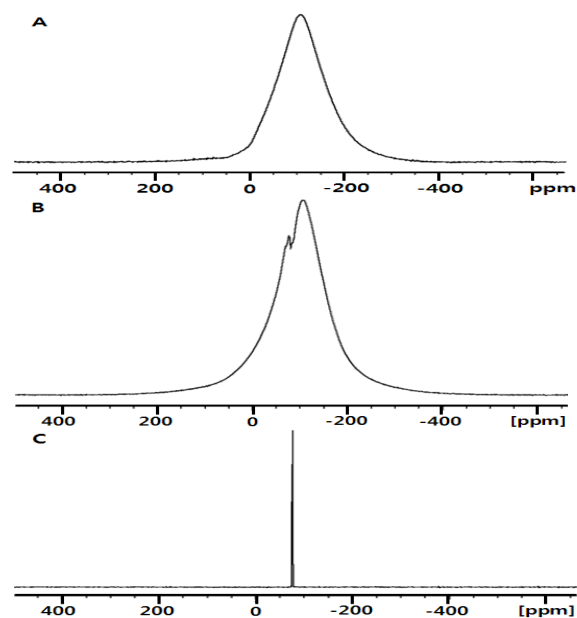

Figure 4. The ^{19}F background signal from the commercialized probe (a) is shown. There is no sample in the receiver coil of probe. A ^{19}F pulse field strength of 62.5 kHz was used. The number of scans was 16. The ^{19}F NMR spectrum with a sample of tri-fluoroethanol (TFE) in the FC400A probe (b) was observed. The broad background signal was overlapped with the sharp signal of TFE shown at about -77 ppm. The signal of TFE could not be distinguished from the huge background signal. A ^{19}F pulse field strength of 52.1 kHz was used, and the number of scans is 1. (c) The ^{19}F spectrum of TFE in the FC400B probe was observed. The broad background signal disappeared, and only a narrow signal of TFE at -77.03 ppm was observed. A ^{19}F pulse field strength of 55.56 kHz was used. The number of scans was 16, and the S/N ratio was 509.

Discussion

The custom-built ^{19}F-^{13}C double-resonance probe with a square flat coil for a 400MHz wide-bore magnet was successfully constructed with high efficiency and performance for the measurement of fluorinated materials like LCD

panels and Li-ion batteries. The ^{19}F background signal from the probe was completely removed, and the probe had high sensitivity and a high radio frequency power capacity. This custom-built probe is sufficient for the in-situ analysis of electronic devices that contain fluorinated materials, and will contribute to promoting the performance of high-tech devices.

Acknowledgements

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