



Solid-state STRAFI NMR probe for material imaging of quadrupolar nuclei

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ARTICLE INFO

Article history:

Received 31 July 2012

Revised 16 October 2012

Available online 26 October 2012

Keywords:

Fringe field

Stray field imaging (STRAFI)

Quadrupolar nuclei

Materials

Magnetic resonance imaging

ABSTRACT

Stray field imaging (STRAFI) has provided an alternative imaging method to study solid materials that are typically difficult to obtain using conventional MRI methods. For small volume samples, image resolution is a challenge since extremely strong gradients are required to examine narrow slices. Here we present a STRAFI probe for imaging materials with quadrupolar nuclei. Experiments were performed on a 19.6 T magnet which has a fringe field gradient strength of 72 T/m, nearly 50 times stronger than commercial microimagers. We demonstrate the ability to acquire ⁷Li 1D profiles of liquid and solid state lithium phantoms with clearly resolved features in the micrometer scale and as a practical example a Li ion battery electrode material is also examined.

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1. Introduction

Magnetic resonance imaging (MRI) can provide valuable information into the stability and uniformity of solid-state materials and benefit many industrial and research applications because of its non-invasive nature. Conventional MRI methods require certain delays or dead times in order to settle the applied gradients. Therefore, NMR signals of the materials being imaged need to have long enough transverse relaxation time (T_2) to ensure that the signals will not significantly decay prior to acquisition. MRI has become very popular in medical research and diagnostics because of its ability to image the flow of the biological matter and/or “soft” tissues. Yet, MRI is an uncommon practice when studying solid materials due to the difficulties in obtaining high resolution images. First, the line widths are significantly broadened in the solid materials due to their intrinsically slow molecular motion. As a result, the T_2 values are extremely short and the sensitivity of solid-state imaging significantly degrades. For instance, solid materials typically contain some quadrupolar nuclei such as ⁷Li, ²⁵Mg, and ^{47/49}Ti, which are crucial elements for their properties and functions, but are highly insensitive to NMR. In addition, their quadrupolar coupling constants could be on the order of MHz which can further reduce their sensitivity. Secondly, there exist some practical difficulties to obtain high resolution images using conventional MRI. In general, for a given gradient strength the imaging resolution is proportional to the line widths. Therefore, a much stronger gradient strength is required to improve the resolu-

tion, which in turn requires more powerful gradient amplifiers and a longer time to regenerate the field homogeneity, further attenuating the observed signals due to the short T_2 value. Here we demonstrate an alternative method suitable for imaging solid materials.

It is generally believed that the spatial resolution Δx can be determined according to [1]:

$$\Delta x = \frac{2\pi\Delta\nu_{1/2}}{\gamma G_z} \quad (1)$$

where $\Delta\nu_{1/2}$ is the peak line-width at half height, G_z is the gradient strength in the z direction, and γ is the gyromagnetic ratio. Reducing the line width of the spectrum is an effective method for improving resolution. In most medical MRI and NMRI studies, samples are composed of liquids or “soft” solids in which the dominant NMR interactions (such as dipolar interactions) are averaged out, resulting in relatively sharp NMR spectra. For rigid solids, numerous NMR interactions (e.g. chemical shielding, quadrupolar and dipolar) contribute to line broadening reducing the resolution. High resolution solid-state NMR methods such as magic angle spinning [2–4] and line-narrowing pulse sequences [5–10] have successfully been used with imaging experiments to reduce or eliminate those interactions. In cases where high spinning speeds are not achievable or pulse sequences do not efficiently reduce the NMR interactions other approaches must be considered. An alternative option is to use large gradient strengths. The gradient strength becomes the dominating factor that dictates the intrinsic line width of the nuclei and, hence, the resolution of the image. With conventional MRI hardware, the requirements to produce large gradients may not be met due to the high power demands. Microimagers are typically used for small samples and with their smaller gradient coils, strong gradients are

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easily attainable (up to 1.5 T/m commercially). However, the problem associated with short T_2 values remains especially when longer delays are needed to settle stronger gradients. Moreover, proper gradient amplifiers and specialized probes are required which may increase expenses.

Samoilenko et al. introduced an alternative solid imaging method which exploits the strong gradients in the fringe field of superconducting magnets [11]. The natural field gradient eliminates the need for gradient coils and amplifiers. The combination of short radio frequency pulses and extremely strong field gradients can produce images with higher resolutions than those currently obtained with the conventional MRI setups. By using a static magnetic field gradient there is no need for settling delays, as when applying gradient pulses in the MRI experiments, which will benefit materials with short T_2 values. Stray field imaging (STRAFI) has been used to study thin films [12–22], paramagnetic samples [23–25], water content of soil samples [26–31], various dental materials [32–43], and for diffusion experiments [44–48]. Thus far, ^1H STRAFI experiments are employed most often and only a few low-gamma nuclei STRAFI studies have been published [24,49–54].

STRAFI provides many advantages over conventional MRI methods to study solid materials. The natural presence of stray field gradients with superconducting magnets eliminates the need for high power gradient amps to produce the strong gradients required for narrow slice selectivity. Signal enhancement can be achieved by using the Long Echo Train Summation (LETS) method [51,54]. The repetition of a series of refocusing pulses, as in the CPMG sequence, allow for the collection of numerous echoes which are summed together providing a boost in signal sensitivity. In addition, if the delay between pulses is short enough, the collection of pulses serves as a spin lock allowing the magnetization to relax with respect to $T_{1\rho}$ rather than T_2 . The prolonged relaxation with the echo train will aid in the implementation of shaped pulses to help improve image resolution.

Shaped pulses are a common practice with NMR and MRI experiments [55]. In addition to fewer artifacts and better reproducibility, excitation profiles can be manipulated for enhanced slice selectivity. Sinc and Hermite pulses are often utilized in MRI because the Fourier transform of these shapes result in a rectangular function [56,57]. Gaussian shapes are also favorable as opposed to rectangular pulses since there are no side lobes in the excitation profile [58]. By eliminating any off-resonance artifacts adjacent slices will be unaffected. More recently, it has been shown that shaped pulses can also improve line shapes and slice resolution when used in stray field experiments [59].

Here, we present a high resolution solid-state STRAFI NMR probe for material imaging of quadrupolar nuclei. We discuss aspects of setting up such experiments and explore the practicality of implementing shaped pulses for STRAFI studies to improve slice selectivity. Evaluations are conducted through ^7Li STRAFI experiments on various lithium liquid and solid phantoms. The acquisition of high resolution images of solid-state materials, such as Li-ion battery electrodes, is also demonstrated.

2. Experimental

2.1. Battery electrode preparation

LiCoO_2 electrode was made by thoroughly mixing 90 wt% of LiCoO_2 with 5 wt% acetylene black powders. 5 wt% polytetrafluoroethylene (PTFE) was then added until the mixture was uniform. The material was then rolled by hand for further mixing and flattened to the desired thickness using a rolling press. The sheet was then dried in an oven at 120 °C for 0.5 h. Disks were cut with a 6.75 mm diameter then placed in an oven overnight for further drying.

2.2. STRAFI experiments

All STRAFI experiments were conducted on a Magnex 19.6 T ultra-narrow bore (29 mm) superconducting magnet using a Bruker DRX console. The translational movement of the sample was controlled using a stepper motor. The sample was initially brought to a predetermined reference point and then raised to a start position to be imaged. After the movement settled down for 300 ms, a quadrupolar echo sequence was applied to acquire a number of echoes. Immediately after, the stepper motor translated the sample to the next position for signal acquisition and repeated this movement until the last point to be imaged was reached. The stepper motor then moved the sample back to the start position and repeated this procedure for signal accumulation. A home built triggering device was used to control such movements in synchronization with the pulse sequence used for the STRAFI experiments. A MATLAB program was used to convert the echo intensities into one-dimensional (1D) STRAFI profiles [60].

The opposite phase $[90_x-\tau-(90_y-\tau-\text{acq}-\tau)_N]$ (Seq.1) or same phase $[90_x-\tau-(90_x-\tau-\text{acq}-\tau)_N]$ (Seq.2) quadrupole echo sequences were used where $N=8$. Pulse calibrations were performed using a concentrated sample of LiBr in D_2O . 90° flip angles were confirmed using both Seq.1 and Seq.2 as described by Randall [61]. Shaped pulses were generated using the pulse shape utility provided with the Bruker XWINNMR software package. Gaussian, Sinc with 0 (Sinc0) and 1 (Sinc1) side lobe, and Hermite shaped pulses were examined. All pulses were created with 100 points to accommodate short pulse lengths. In order to maintain the same excitation bandwidth at a common power level, pulse width scaling factors (Ω_{sp}) with respect to rectangular pulses were estimated using the Bruker's pulse shape utility. Ω_{sp} for Gaussian, Sinc0, Sinc1, and Hermite pulses are 2.14, 1.62, 3.72, and 4.46, respectively. Pulse lengths were then optimized with Seq.2 to exhibit the standard pattern of a proper 90° flip angle [62].

3. Probe design

3.1. Resonant coil tests

For STRAFI experiments on superconducting NMR magnets, the most convenient way to translate the sample is by moving it along the z -axis of $\mathbf{B}_0$, therefore a transverse resonator is required. Three common transverse coils are the Alderman-Grant (AG), saddle and birdcage coils. For our tests we chose to examine the AG and saddle coils because of the ease of tuning a broad frequency range with minimal circuit modifications for initial STRAFI setup and tests. The use of the birdcage coil for STRAFI experiments is not explored here due to complications in tuning the circuit. For instance, to attain high B_1 field homogeneity a high number of legs on the birdcage coil is required, which reduces the tuning range. Tuning is often done by adjusting the capacitance along one or two of the legs but leads to angular asymmetry [63,64].

Due to size constraints with ultra-narrow bore probes, the outer diameter of the coil is restricted to be no more than 12 mm; an inner diameter of 10.25 ± 0.05 mm was selected and a 0.25 mm thick copper foil was used to maintain a rigid structure. Dimensions of an AG coil typically has a length (l) to diameter (d) ratio between 1 and 1.5 and a 90° window angle [65]. For saddle coils, $l/d=1.66$ and a window angle of 135° are optimal dimensions [66,67]. However, these dimensions are selected to find a uniform field across a majority of the coil. For STRAFI experiments having a uniform B_1 field in the z direction is unnecessary since only a thin slice of the sample is excited at one time. Reducing the height of the coil will increase the sample filling factor and will improve sensitivity [68]. Moreover, different from traditional STRAFI coil

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