Efficient Low-γ Solid State NMR Probe for Material Chemistry Applications

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Introduction

We developed a *Low-G* MAS NMR probe that fills the void in low-γ probe technology and enables sensitive low-γ NMR for many energy and material chemistry applications that require ^{1}H channel for cross-polarization and decoupling. This development focuses on solid state NMR of low-γ nuclei such as ^{39}K, ^{25}Mg, ^{43}Ca, ^{87}Sr, ^{135,137}Ba, ^{67}Zn, ^{35,37}Cl, ^{33}S, and many others. These elements play important roles in glasses, catalysts and battery materials but are difficult to observe by NMR due to low NMR frequencies, low natural abundances and large quadrupolar interactions. Today's multi-channel commercial MAS probes for material chemistry employ single detection coil along with few traps separating ^{1}H and low-gamma circuits. The losses in these traps inevitably place limits on S/N of detection.

Our broadband 4-mm double resonance ^{1}H–X MAS probe is derived from an orthogonal-coil Low-E probe design hat was recently developed for biological applications [1,2]. Original Low-E development was driven by the need to protect biological samples from rf-induced heating – something that most material chemists have little concern for. However, it is the exceptional sensitivity of low-γ detection channel in these probes that is often missed and that can be crucial for recovery of S/N in low-γ MAS experiments at high fields. The S/N boost resulting from using 2 orthogonal coils and having no ^{1}H traps in rf circuit makes broadband Low-E derivative (thereafter referred to as Low-G) very attractive for low-γ detection.

Figure 1. Broadband tuning using sliding PC boards.

Results and Discussion

The 800 MHz Low-G probe presented here is a joint collaboration with Lille University, France. The broadband tuning feature of this 4-mm double resonance ^{1}H–X MAS probe is implemented through sliding inserts (**Figure 1**). Using combination of inserts, detection channel can be tuned to most of the periodic table (^{109}Ag...^{81}Br). The probe was constructed at NHMFL and installed at Lille University 800 MHz NMR facility. Preliminary results indicate excellent RF efficiency in probe's detection channel: ^{17}O B_1 = 95 kHz @ 492 W (s=½ equivalent), ^{25}Mg B_1= 50 kHz @ 645 W (s=½ equiv.), ^{1}H decoupling B_1 = 100 kHz x 10ms+ @ 375 Watt. Sensitivity comparison (**Figure 2**) was performed on ZnO with commercial 7 mm ^{1}H–X broadband Bruker MAS probe provided at the same spectrometer. Note that a 7 mm rotor packs many times more sample than a 4 mm one. Nevertheless, under identical experimental conditions, the 4 mm Low-G probe yields S/N almost comparable to the 7 mm commercial probe, while providing user with much higher limits of rf field and MAS spinning speeds. A Hall sensor incorporated into the spinner allows repeated setting of magic angle within 0.001° to aid with angle-sensitive STMAS experiments.

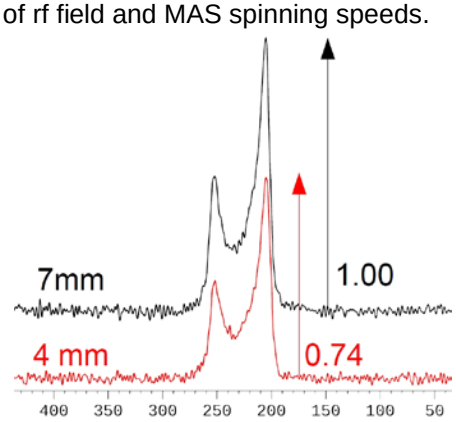

Figure 2. ^{67}Zn S/N comparison between 4 mm Low-G and 7 mm Bruker commercial ^{1}H–X MAS probes, 18.8 Tesla. ZnO sample, static, 1-pulse, 7200 transients. Same noise level for each probe. 4 mm Low-G probe yields nearly same S/N as 7 mm Bruker probe despite huge difference in sample volume.

Conclusions

MAS NMR probes built using orthogonal coil designs like Low-E and others [1-4] can boost detection sensitivity for low-γ nuclei and we expect them to be of interest to material chemists. We demonstrated adaptation of Low-E technology for non-biological, high-field material chemistry applications, with sliding inserts allowing for broadband X tuning.

Acknowledgements

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References

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