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Stability Enhancement of ^{129}Xe Hyperpolarizing System Using Alkali Metal Vapor in Spin-Exchange Optical Pumping Cell to Achieve High NMR Sensitivity

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Hyperpolarized (HP) ^{129}Xe NMR and MRI have enabled ^{129}Xe studies with extraordinarily enhanced sensitivity, stimulating new developments in magnetic resonance in chemistry, physics, biology and medicine. However, the standard method of HP ^{129}Xe production inevitably demands Rb vapor for the excitation, which has made the method very sensitive to impurities such as water or oxygen. This is the case especially in the recirculating system. In the present study, stability of the hyperpolarizing system is discussed by proposing the “cell decay constant”, which symbolizes the decay rate of the NMR signal obtained from the system. The cell decay constant is effectively decreased to 1/3 by introducing separated chambers and mechanical stirring of the alkali metals used in the system, making it effective for accumulating FIDs over 30 to 100 h. The newly developed hyperpolarizing system has been successfully applied for newly detecting a broad signal at 190 ppm with an industrial material Nanofiber.

Keywords Hyperpolarized, ^{129}Xe , NMR, Rb degradation, cell decay constant, SN improvement, Nanofiber

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Introduction

Recently, hyperpolarized (HP) nuclei have attracted widespread attention in NMR and MRI because of their ability to resolve the long-standing problem of low sensitivity in magnetic resonance.^{1,2} Among the different types of HP nuclei, such as ^3He , ^{129}Xe , ^{83}Kr , ^{13}C , ^{15}N , ^{107}Ag , and ^{109}Ag , ^3He and ^{129}Xe , the noble gases, are characterized by an ability to detect gas phase signals directly. This is quite useful for the clarification of structures and functions of void spaces not only in living bodies such as lungs but also in porous materials such as zeolites.^{3,4} HP ^{129}Xe is also utilized in Hyper-CEST (Chemical Exchange Saturation Transfer) experiments to detect very low, pico- to femto-molar molecules of biomedical interest in solution.^{5,6} It has also been determined to be useful as a high-sensitivity detector of weak magnetic field, which surpasses SQUID (Superconducting Quantum Interference Device) in detection limit and accessibility.^{7,8} Among the noble gases, ^{129}Xe offers the benefits of easier hyperpolarization through SEOP (Spin Exchange Optical Pumping) with lower cost for the raw material gas, and it seems that it could be the key to widespread use of HP gas in NMR and MRI. In order to save Xe gas consumption in experiments with long operation times, such as 2D-NMR or signal averaging to detect very weak peaks, a recirculating

system is exploited with basically successful results.^{9,10} However, the HP noble gas has not gained wide acceptance for clinical use as one of the gas media like the anesthesia Xe gas, despite basic studies over a quarter century after the first application to void space analysis with excised mouse lungs.^{11,12} Similarly, widespread use of the HP gas has not been realized until now in materials analysis, although potential significance of the HP gas in surface science and catalysis has been pointed out as early as 1991.¹³ Therefore, critical evaluation of the performance in a hyperpolarizing system seems necessary in order to promote widespread acceptance as an analytical tool in different fields of science and industry. In the present study, stability enhancement of the system is attempted, focusing on the role and property of the alkali metal used in the SEOP method, especially in the recirculating mode. The hyperpolarizing system is newly developed in the recirculating mode and the stability is tested on the sample of HF capsule, which is considered to evolve spurious water vapor under the flow of highly dried gas, and the Nanofiber, which is expected to adsorb Xe gas on the nano-porous surface. No reports of the above were available as of this writing.

Experimental

Hyperpolarizing system

A schematic drawing of the recirculating system is shown in Fig. 1. The hyperpolarizing pumping cell (HPC in Fig. 1), sized

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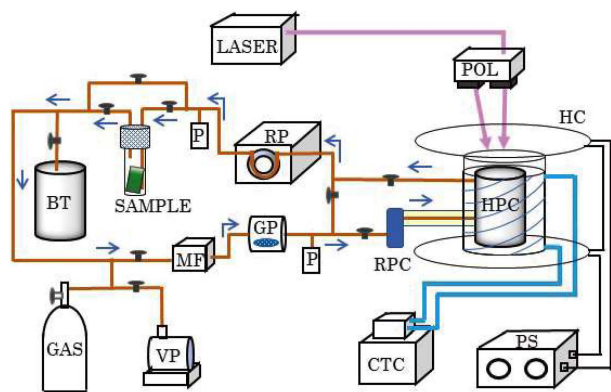


Fig. 1 Total view of the ^{129}Xe hyperpolarizing system operating under gas recirculation mode. BT = Buffer Tank, CTC = Temperature Controller for Oil Bath, GAS = Gas Storage Cylinder, GP = Gas Purifier, HC = Helmholtz Coil, HPC = Hyperpolarizing Pumping Cell immersed in Oil Bath, LASER = Laser Source, MF = Mass Flow Controller, P = Pressure Gauge, POL = Optical Polarizer with $1/4\lambda$ Plates, PS = Power Supply, RPC = Rb Preliminary Chamber, RP = Roller Pump, VP = Vacuum Pump. The arrow \rightarrow denotes gas flow in the recirculation mode.

50 mm in diameter and 200 mm in length, was immersed in an oil bath controlled at 110°C so that the cell upper window was located 30 – 40 mm underneath the oil surface, and a magnetic field of 26 mT was applied from the Helmholtz coil Lakeshore MH-12 (HC in Fig. 1). The broadband laser diode array, COHERENT FAP system, provided 60 W output and 794.7 nm wavelength beam with 2 – 3 nm FWHM (Full Width at Half Maximum), and was used for the excitation in the HPC after changing to a circularly polarized beam through an optical polarizer (POL). A mixed gas of 90% Xe, natural abundance gas from Air Liquide Japan Ltd., Tokyo, and 10% N_2 by volume was flowed into the HPC at the rate of 34 or 68 mL/min under the control of the roller pump RP-11, FURUE Co., Ltd., Tokyo, (RP), and the mass flow controller Model 5100 Series, KOFLOC Co., Ltd., Tokyo, (MF). The pressures in the HPC and the 10ϕ NMR sample tube (SAMPLE) were set near 0.015 and 0.1 MPa, respectively, by adjusting the total gas volume initially loaded and the roller rotation rate of RP. The HP gas was flowed into the 10ϕ NMR sample tube from the bottom through a glass capillary.

About 0.5 g Rb was deposited in the HPC together with several glass beads with 2 – 3 mm diameter to assist manual agitation of Rb, which was done to maintain the metal specular gloss at the beginning of a new NMR experiment as needed.

As described below in the Methods and Calculations section, two separated chambers were introduced in front of the HPC: in one separated chamber (GP in Fig. 2) K-Na alloy was filled to sensitively remove contaminant gasses possibly invading into the recirculating system, and in another one (RPC in Fig. 2) Rb was deposited and heated to maintain preliminary vaporization.

In the present study broad band laser was used and higher content of 90% Xe gas was adopted for direct recirculation of the HP gas, and the polarization reached was 1.3%. If Xe content is reduced to 5%, polarization will be enhanced to higher values such as 31 – 64%.¹⁴ However, since NMR signal intensity is proportional to the polarization multiplied by ^{129}Xe gas content in the direct recirculation experiment, higher Xe content is suited for higher SN ratio. Furthermore, N_2 can act as an alternative adsorbate to the sample and lower N_2 content may be recommended in surface studies; hence higher content of 90% Xe was selected in the present study.

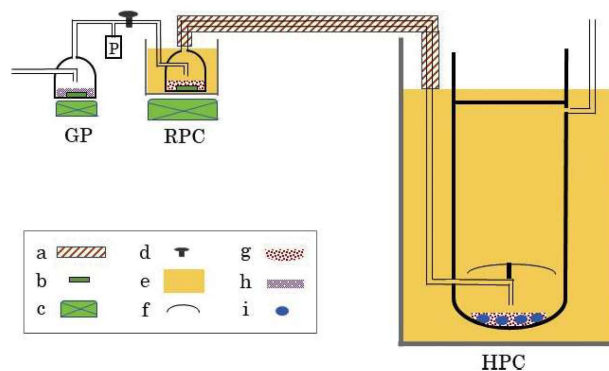


Fig. 2 Schematic drawing of the hyperpolarizing cell HPC and two separated chambers GP and RPC. K-Na alloy in GP and Rb metal in RPC are mechanically stirred. a = Rb vapor transfer tube with electrical heater, b = stirrer bar, c = magnetic stirrer, d = stop cock, e = oil bath, f = glass roof for Rb vaporizing section, g = Rb in RPC and HPC, h = K-Na alloy in GP, i = glass bead.

NMR experiments

NMR spectra were measured on a 9.4 T Agilent Unity INOVA 400WB system with the resonance frequency of 110.6 MHz for ^{129}Xe at ambient temperature.

Statistical data analysis

In order to determine the cell decay constant from the NMR signal decay curve obtained from repeated measurements of NMR spectra over several tens of hours, the least-squares fit based on the Levenberg–Marquardt algorithm was made on the program ORIGIN supplied from Lightstone Co., Tokyo.

Materials for NMR measurement

HF Capsule: Gelatin capsule #2 supplied from Matsuya Co., Osaka. The capsule was cut to *ca.* 3×10 mm strips and filled into the 10ϕ NMR tube.

Nanofiber: Ultra fine polyester fiber with 700 nm diameter supplied by Teijin Frontier Co., Ltd., Osaka.

Methods and Calculations

Basic design of the hyperpolarizing system

To enhance the stable operation of the hyperpolarizing system by preventing degradation of the HPC as much as possible and ensure easy access to HP ^{129}Xe gas for NMR and MRI, we attempt to develop a new system that is tolerable to experiments with long operation times in materials analysis by 1D and 2D NMR as well as small animal imaging by MRI. The Rb vapor, which works as a catalyst in the essential process of spin transfer from circularly polarized photons to the noble gas nuclei, is extremely sensitive to moisture or oxygen in the atmosphere, and hence the metal becomes corrupted as a catalyst immediately once trace amounts of these contaminant gases enter into the hyperpolarizing system. Furthermore, in the recirculating system, a trace amount of the contaminant gases can evolve from the sample even if the sample is pre-purified. Therefore, a first prerequisite for stable operation is to secure the system against contaminants. As for the second prerequisite, stable Rb vapor pressure in the HPC is indispensable for a stable NMR output signal. In the present study, in order to satisfy these two prerequisites, two separated chambers are introduced prior to the HPC (Fig. 2). The first one, GP, includes K-Na alloy, which

can remove gases reactive with Rb very effectively compared to other agents, such as silica gel or zeolites; the alloy is liquid at room temperature and easily stirred to maintain a specular gloss on the surface that is a good indicator of the impurity-removing power. The second one, RPC, includes Rb metal, which is heated to the same temperature as that in the HPC and stirred to maintain stable Rb vaporization as judged by the metallic gloss on the Rb surface under the Xe gas flow. These two separated chambers are located apart from the Helmholtz coil so that the stirrers do not disturb the magnetic field generated by the coil. At the same time, Rb in the HPC needs to be placed in a homogeneous magnetic field and cannot be stirred magnetically, and hence it is agitated by manual shaking of the cell as needed at the beginning of a new experiment.

Evaluation of the hyperpolarizing system

Several parameters, such as ^{129}Xe spin polarization, production rate of the HP gas, and ^{129}Xe content in the HP gas, are useful in evaluating the performance of a hyperpolarizing system. Spin polarization has been improved considerably and maximum polarization is realized with the aid of a narrowband laser.¹⁵ In the recirculating system, especially, extra contamination can take place throughout the process of recirculation, which causes extra decay in the output signal in NMR experiments. Hitherto, however, discussions on this property have not been provided and detailed quantitative analysis will be necessary for the development of a robust and sustainable hyperpolarizing system. The authors propose that this type of property can be treated by the decay time constant that represents an exponential decay of the output signal.

When FIDs are accumulated to further enhance the SN ratio in the HP nuclei experiments under the condition of exponential decay in the NMR signal supplied from the pumping cell, the SN ratio in the j -th single spectrum is expressed as follows,

$$SN(j) = SN^0 e^{-aj} \quad (1)$$

where SN^0 means the SN ratio at the beginning of accumulation and a is the cell decay constant. After the accumulation of n FIDs, the resulting SN ratio $SN^{(n)}$ can be calculated in the following manner,

$$\begin{aligned} SN^{(n)} &= \frac{\sum_{j=1}^n SN^0 e^{-aj}}{\sqrt{n}} = \frac{SN^0}{\sqrt{n}} (e^{-a} + e^{-2a} + e^{-3a} \dots + e^{-na}) \\ &= \frac{SN^0}{\sqrt{n}} e^{-a} \frac{1 - e^{-na}}{1 - e^{-a}} = \frac{SN^0}{\sqrt{n}} \frac{1 - e^{-na}}{e^a - 1} \end{aligned} \quad (2)$$

To obtain the value of n that maximize $SN^{(n)}$, derivative of Eq. (2) is calculated and set to zero, leading to a relation,

$$\frac{(2na+1)}{e^{na}} = 1 \quad (3)$$

which can be solved by manual calculation and gives a solution $na = 1.2565$ (Table S1, Supporting Information).

When the cell decay constant is defined as b on the time scale instead of a on the accumulation number scale, Eq. (4) is given,

$$S(t) = S_0 e^{-bt} \quad (4)$$

where S means the signal intensity and S^0 is the initial signal intensity at $t = 0$, and $a = bR$ holds where R is the repetition time of signal accumulation. Here, total time of accumulation t_t is given as $t_t = nR$, and hence the relation $na = 1.2565$ changes to $bt_t = 1.2565$. In this way the cell decay constant b can be

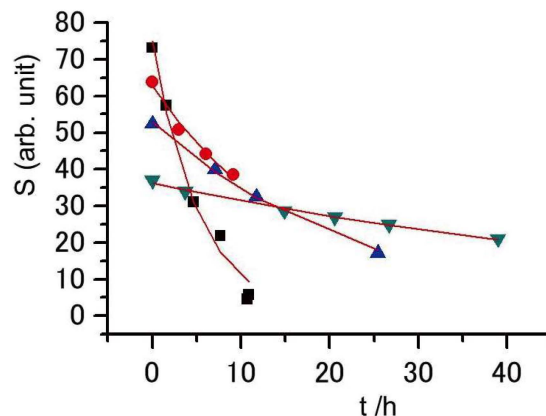


Fig. 3 ^{129}Xe decay curves to obtain the cell decay time constant b in Eq. (4). ■ Sample: HF Capsule 0.18 g. Rb is not stirred in the separated chamber. ● Sample: HF Capsule 0.18 g. Rb is stirred in the separated chamber. ▲ No sample in NMR tube. Rb is not stirred in the separated chamber. ▼ No sample in NMR tube. Rb is stirred in the separated chamber.

Table 1 Least squares fit of the experimental decay curves by Eq. (4)^a

Sample	Rb stirrer	S^0	b/h	$t_t = 1.2565/b$	Decay curve
HF capsule	OFF (cold)	75.1 ± 3.6	0.192 ± 0.018	6.5 h	Fig. 3 ■
HF capsule	ON (hot)	62.7 ± 1.7	0.057 ± 0.006	22.0 h	Fig. 3 ●
No sample	OFF (cold)	53.0 ± 0.8	0.043 ± 0.002	29.2 h	Fig. 3 ▲
No sample	ON (hot)	36.3 ± 0.4	0.014 ± 0.001	89.8 h	Fig. 3 ▼

a. When Rb stirrer is ON, Rb is liquid at 110°C , otherwise it is solid at room temperature. S^0 is given in arbitrary unit. The unit h means hour.

seen to represent the effective operation time of the hyperpolarizing system.

Results and Discussion

Effect of mechanical stirring of Rb on the performance of the hyperpolarizing system was tested as shown in Fig. 3, where the NMR signal was monitored with and without the mechanical stirring of Rb in the separated chamber. The least-squares fit to obtain the cell decay time constant b based on Eq. (4) is summarized in Table 1. When the 0.18 g HF capsule was filled in a 10ϕ NMR tube, the cell decay constant was reduced from 0.192/h under no stirring to 0.057/h under stirring, indicating a 3.4-fold improvement by mechanical stirring. When measurements were made with an empty 10ϕ NMR tube, the cell constant was reduced from 0.043/h under no stirring to 0.014/h under stirring, supporting a 3.1-fold improvement by mechanical stirring. Therefore, mechanical stirring of Rb is seen to elongate the effective operation time of the hyperpolarizing system by more than 3-fold. The condition of $bt_t = 1.2565$ for the maximum SN ratio tells us that the SN ratio will be improved up to the total accumulation time of $t_t = 6.5$ h, 22.0 h, 29.2 h, and 89.8 h for the case of ■, ●, ▲, and ▼ in Fig. 3, respectively. The shorter t_t values for ■ compared to ▲ and for ● compared to ▼ may be caused by a spurious evolution of impurity gases such as water from the sample. Gradual evolution of impurity gases can affect the performance of the

total hyperpolarizing system for a long time even if extensive care has been given to prevent the degradation effect. Detailed evaluation of the hyperpolarizing system by the decay curve analysis is shown to be useful in detecting such a degradation effect sensitively and quantitatively.

Sometimes Rb is deposited in a reservoir¹⁰ or inlet arm¹⁶ directly attached to the pumping cell. But such a device is considered to be a part of the pumping cell. In the present study the Rb container, separated chamber, is placed apart from the pumping cell that has made the mechanical stirring acceptable without disturbing the magnetic field applied to the pumping cell. The stirring effect is proposed, evidenced and quantitatively analyzed in the present study for the first time, including in the separated chamber as well as in the pumping cell.

Equation (2) is further simplified as,

$$SN^{(n)} = SN^0 \sqrt{n} \frac{1 - e^{-na}}{na} \quad (5)$$

since a , in the unit of /s, is very small compared to 1.0 and $e^a = 1 + a$ holds with good accuracy. Here, SN^0 is the SN ratio reached after accumulation of n FIDs in the standard accumulation without systematic decay in every NMR signal. Therefore, the factor $(1 - e^{-na})/na$ denotes the reduction in SN caused by the decay in every accumulated signal. Accordingly, this may be called “cell degradation factor” for the SN improvement in HP nuclei experiments. This factor amounts to 0.57 when the maximum optimal number of accumulation is reached and $na = 1.2565$ holds. That is, cell degradation reduces the SN improvement to 57% compared to that without degradation. This 43% reduction caused by the cell degradation seems minor compared to the enhancement factor of the HP technique, which amounts to as much as the order of 10^4 . This clearly shows the potential of excellent utility of the recirculating system in detecting very weak signals as long as the Rb degradation is fully protected and the cell decay constant b is made so small that the total accumulation time predicted from the relation $t_1 = 1.2565/b$ covers the necessary accumulation time.

Next, our new hyperpolarizing system was applied to detect a very weak signal of ^{129}Xe adsorbed on the fiber of an industrial product. Figure 4 shows the HP ^{129}Xe NMR spectra of 0.05 g Nanofiber filled in a 10ϕ NMR tube, to which the HP Xe gas containing 90% natural abundance Xe and 10% N_2 was flowed from the bottom at a rate of 34 mL/min. Before the development of our new hyperpolarizing system, it was difficult to identify any adsorbed peaks from the sample except the gas phase peak at 0 ppm even after the accumulation of 47070 FIDs by the standard pulse sequence (Fig. 4a) and after that of 64496 FIDs by the advanced binominal pulse sequence designed to suppress strong solvent (gaseous) peak (Fig. 4b).¹⁷ In the binominal spectrum, a phase distorted peak at 0 ppm shows an incomplete cancellation of the strong gas peak in the binominal sequence after long time accumulation. A very broad peak could be suggested near 200 ppm in Fig. 4b, but the spectral pattern changes drastically by phase adjustment and it is difficult to identify any peak near 200 ppm from this spectrum. Remeasurement by the new hyperpolarizing system has given the binominal spectrum (Fig. 4c) after accumulation of 10816 FIDs, in which a broad peak is clearly observed at 190 ppm with the FWHM linewidth 72 ppm. A very broad signal was reported for ^{129}Xe adsorbed on the surface of poly(acrylic acid), where the broadening was considered to be due to the chemical shift effect from the surface water since the line width was reduced greatly after heating at 80°C under vacuum overnight.¹⁸

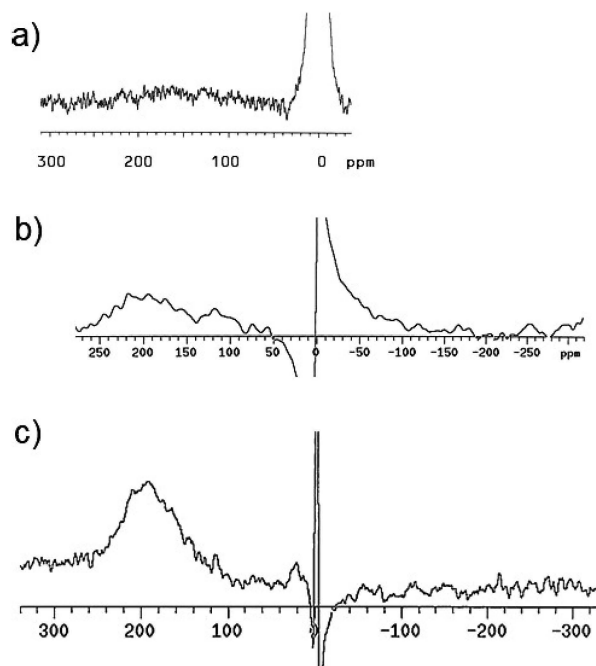


Fig. 4 Successful detection of the ^{129}Xe peak near 190 ppm from Nanofiber by the new hyperpolarizing system. a) and b): Unsuccessful results measured before the development of the new recirculating system without Rb separated chamber and stirring of Rb. The pulse sequences used are standard one in a) and binom in b). c): Successful observation by the new recirculating system using binom sequence. The horizontal frequency axis is doubled in the measurement of the binom spectrum. Measurement conditions: a) sw (spectral width) = 40 kHz, pw (pulse width) = 10 μs (55° pulse), at (acquisition time) = 0.1 s, d1 (delay time after acquisition) = 0.3 s, lb (window function, line broadening) = 100 Hz. b) sw = 70 kHz, offset (offset frequency in binom sequence where the signal is most effectively enhanced) = 20 kHz, pw = 64 μs , tpwr (transmitter power) = 43 db (reduced by 12 db from 55 db), at = 0.05 s, d1 = 0.2 s, lb = 1000 Hz, ct (accumulated number of FID) = 64496. c) sw = 100 kHz, offset = 20 kHz, pw = 64 μs , tpwr = 43 db, at = 0.1 s, d1 = 1 s, lb = 300 Hz, ct = 10816.

In the present study, however, the signal was unchanged after such a heating, and further detailed study is necessary to examine the broadening effect.

The newly developed long-life hyperpolarizing system will promote widespread use of NMR and MRI in different fields of surface, void space, and dissolved phase analyses in materials science. Its use will be more critical in experiments where isotopically enriched ^{129}Xe is resorted to enhance the basic sensitivity. The new system will also be useful to elongate the stable and effective operation time of Rb for the hyperpolarizing system in medical MRI where a large amount of HP ^{129}Xe gas is once solidified to separate from foreign gases and transferred to a reservoir bag before use.

Conclusions

We have developed the recirculating ^{129}Xe hyperpolarizing system that ensures high performance by introducing the two separated chambers that include alkali metals for purification and pre-vaporization of Rb, where mechanical stirring can be made without disturbing the magnetic field applied to the pumping cell. The new system has succeeded in preventing the

pumping cell degradation considerably so that the effective operation time of 30–100 h is realized with the SN ratio improvement of 57% compared to the case without the cell degradation. Application to an industrial material, Nanofiber, has supported the usefulness of the new system through the detection of a very broad signal at 190 ppm with FWHM 72 ppm.

Acknowledgements

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Supporting Information

Table S1: Solving Eq. (3) by manual calculation. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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