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

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Abstract

Hyperpolarized (HP) $^{129}$Xe NMR and MRI have enabled the $^{129}$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 pre-chambers and mechanical stirring of the alkali metals used in the system, making it effective to accumulate FIDs over 30 to 100 hours. The hyperpolarizing system newly developed has succeeded in disclosing the new signal at 190 ppm with an industrial material Nanofiber.

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

Recently hyperpolarized (HP) nuclei have attracted widespread attentions in NMR and MRI because of their ability to resolve historical problem of low sensitivity in magnetic resonance.\(^1,2\) Among the different types of HP nuclei such as \(^3\)He, \(^{129}\)Xe, \(^{85}\)Kr, \(^{13}\)C, \(^{15}\)N, \(^{107}\)Ag, and \(^{109}\)Ag, \(^3\)He 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, biomedically interested molecules in solution.\(^5,6\) It is also investigated to be utilized as a high-sensitivity detector of weak magnetic field which surpasses SQUID (Superconducting Quantum Interference Device) in the detection limit and accessibility.\(^7,8\) Among the noble gases \(^{129}\)Xe reaps the benefits of easier hyperpolarization through SEOP (Spin Exchange Optical Pumping) with lower cost for the raw material gas, and surely holds the key to widespread use of the HP gas NMR and MRI. In order to save Xe gas consumption in long time experiments 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 in spite of the active 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 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 but no reports are available now.

**Experimental**

*Hyperpolarizing system*

A schematic drawing of the recirculating system is shown in Fig. 1. The hyperpolarizing pumping cell (HPC in Fig. 1) sized 50 mm diameter and 200 mm 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) which was used for the excitation in HPC after changed to 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% N₂ by volume was flowed into 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 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 0.5g Rb was deposited in 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 new NMR experiment as needed.
As described below in the Methods and Calculations section two pre-chambers were introduced prior to HPC: in one pre-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 vaporize preliminarily.

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%.\(^1\) However, since NMR signal intensity is proportional to the polarization multiplied by \(^{129}\text{Xe}\) gas content in the direct recirculation experiment, higher Xe content is suited for higher SN ratio. Furthermore, \(\text{N}_2\) can act as an alternative adsorbate to sample and lower \(\text{N}_2\) content may be recommended in surface studies; hence higher content of 90% Xe was selected in the present study.\(^2\)

**NMR experiments**

NMR spectra were measured on 9.4 T Agilent Unity INOVA 400WB system with the resonance frequency of 110.6 MHz for \(^{129}\text{Xe}\) 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 a few ten hours, the least-squares fit based on 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. Capsule was cut to ca. 3×10 mm strips and filled into the 10ający NMR tube.

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

Methods and Calculations

Basic Design of the Hyperpolarizing System

To enhance the stable operation of hyperpolarizing system by preventing degradation of HPC as much as possible and ensure easy access to HP 129Xe gas for NMR and MRI, we attempt to develop a new system which is tolerable to long time experiments 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 atmosphere, and hence the metal becomes spoiled 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 be evolved from the sample even if the sample is pre-purified. Therefore, it is the first prerequisite for the stable operation to secure the system against the spoiling contaminants. As for the second prerequisite, stable Rb vapor pressure in HPC is indispensable to the stable NMR output signal. In the present study, in order to satisfy these two prerequisites two pre-chambers are introduced prior to 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 specular gloss on the surface that is a sharp scale of the impurity-removing power. The second one RPC includes Rb metal which is heated to the same temperature as that in HPC and stirred...
to maintain the stable Rb vaporization as judged by the metallic gloss on Rb surface under the Xe gas flow. These two pre-chambers are located apart from the Helmholtz coil so that the stirrers do not disturb the magnetic field generated by the coil. On this contrary, Rb in HPC needs to be placed in a homogeneous magnetic field and is unable to be stirred magnetically, and hence it is agitated by manual shaking of the cell as needed at the beginning of 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 much until now and maximum polarization is realized with the aid of narrowband laser.\(^\text{15}\) 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 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,

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

(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 $SN^n(0)$ can be calculated in the following manner,

$$SN^n(0) = \frac{\Sigma_{i=1}^{n} SN^0 e^{-ai}}{\sqrt{n}} = \frac{SN^0}{\sqrt{n}} \left(e^{-a} + e^{-2a} + e^{-3a} + \cdots + e^{-na}\right)$$
To obtain the value of \( n \) that maximize \( SN^{(n)} \) derivative of Eq. (2) is taken and set to zero, leading to a relation,

\[
\frac{(2na + 1)}{e^{na}} = 1
\]

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,

\[
S(t) = S^0 e^{-bt}
\]

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 \( t_i \) is given as \( t_i = nR \), and hence the relation \( na = 1.2565 \) changes to \( bt_i = 1.2565 \). In this way the cell decay constant \( b \) can be seen to represent the effective operation time of the hyperpolarizing system.

**Results and Discussion**

Effect of mechanical stirring of Rb on the performance of hyperpolarizing system was tested as shown in Fig. 3 where NMR signal was monitored with and without the mechanical stirring of Rb in the pre-chamber. The least-squares fit to obtain the cell decay time constant \( b \) based on Eq. (4) is summarized in Table 1. When 0.18g HF capsule was filled in a 10\( \phi \) NMR tube, the cell decay constant was reduced from 0.192 /h under no stirring to 0.057 /h under stirring, indicating 3.4-fold improvement by mechanical stirring. When measurements were made with an empty 10\( \phi \) NMR tube, the cell constant was reduced from 0.043 /h under no stirring to 0.014 /h under stirring, supporting 3.1-fold improvement by mechanical stirring. Therefore, mechanical stirring of Rb is seen to elongate the effective operation time of hyperpolarizing
system by more than 3-fold. The condition of $bt = 1.2565$ for the maximum SN ratio tells us that SN ratio will be improved up to the total accumulation time of $t = 6.5$ h, 22.0 h, 29.2 h, and 89.8 h for the case of ■, ●, ▲, and ▼ in Fig. 3, respectively. The shorter $t$ 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 payed 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 reservoir$^{10}$ or inlet arm$^{16}$ directly attached to the pumping cell. But such a device is considered to be a part of the pumping cell. In the present study Rb container, pre-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 pre-chamber as well as in the pumping cell.

Equation (2) is further simplified as,

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

(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, $SN^0 \sqrt{n}$ 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 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 HP technique which amount as high 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 $t_r = 1.2565/b$ covers the necessary accumulation time.

Next our new hyperpolarizing system was applied to detect very weak signal of $^{129}$Xe adsorbed on the fiber of industrial product. Fig. 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 under the 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 47,070 FIDs by the standard pulse sequence (Fig. 4 a) and after that of 64,496 FIDs by the advanced binominal pulse sequence designed to suppress strong solvent (gaseous) peak (Fig. 4 b). 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. 4 b, 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. 4 c) after accumulation of 10,816 FIDs, in which 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. In the present study, however, the signal was unchanged after such a heating, and further detailed study is necessary for 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 pre-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 in great deal so that the effective operation time of 30-100 hrs is realized with the SN ratio improvement amounting 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 very broad signal at 190 ppm with FWHM 72 ppm.

**Acknowledgements**

The authors are grateful to Dr. Y. Kobayashi, Teijin Frontier Co. Ltd, Osaka, for the supply of Nanofiber.

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

| Sample        | Rb Stirrer | $S^0$       | $b$/h | $t = 1.2565/b$ | 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.
Figure Captions

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.

Fig. 2  Schematic drawing of the hyperpolarizing cell HPC and two pre-chambers GP and RPC. K-Na alloy in GP and Rb metal in RPC are mechanically stirred.

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 pre-chamber.
- ● Sample: HF Capsule 0.18 g, Rb is stirred in pre-chamber.
- ▲ No sample in NMR tube. Rb is not stirred in pre-chamber.
- ▼ No sample in NMR tube. Rb is stirred in pre-chamber.

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 new recirculating system without Rb pre-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 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 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, $lb$ = 1,000 Hz, $ct$ (accumulated number of FID) = 64,496.  
c) $sw$ = 100 kHz, offset = 20kHz, $pw$ = 64 μs, $tpwr$ = 43 dB, at = 0.1 s, $d1$ = 1 s, $lb$ = 300 Hz, $ct$ = 10,816.
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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 1/4λ Plates, PS= Power Supply, RPC= Rb Preliminary Chamber, RP= Roller Pump, VP= Vacuum Pump. The arrow $\rightarrow$ denotes gas flow in the recirculation mode.
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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= K-Na alloy in GP, h= Rb in RPC and HPC, i= glass bead.
Fig. 3 $^{129}\text{Xe}$ decay curves to obtain the cell decay time constant $b$ in Eq. 4.

- **Sample**: HF Capsule 0.18 g. Rb is not stirred in pre-chamber.
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Graphical Index

A $^{129}$Xe Hyperpolarizing System
Applicable under Long-Time Recirculation Mode

A Broad $^{129}$Xe NMR Signal Newly Detected at 190 ppm with a Nano Fiber
(Upper: Normal Spectrum)