Measurement and Calculation of Relaxation Time T_2 and Diffusion of Gel Electrolytes Based on the $NaClO_4$ Inorganic Salt During Polymerization by NMR Method with Focusing on ^{23}Na and ^{1}H Nuclei

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Abstract. *In the article, the measurement and following calculation of relaxation time T_2 of gel electrolytes based on the $NaClO_4$ inorganic salt and measurement of diffusion coefficients are described. The measurement is focused on ^{1}H and ^{23}Na nuclei. The value of relaxation time T_2 is obtained by approximation of the measured FID (Free Induction Decay) signal with two exponentials using a genetic algorithm. To measure relaxation time T_2, the Hahn echo was used. To measure diffusion, the PFG-SE method (Pulsed Field Gradient Spin) was used. The change of relaxation times and diffusion coefficients during polymerization time indicate a change in the internal structure and chemical composition of gel electrolytes based on $NaClO_4$.*

Keywords: T_2 Relaxation, Diffusion, NMR, Measurement

1. Introduction

Nuclear magnetic resonance spectroscopy is one of the ways to examine the properties of conducting gels based on the $NaClO_4$ inorganic salt during polymerization. For batteries with liquid electrolyte, a key challenge is to replace the liquid electrolyte with solid electrolyte. The main disadvantage of liquid electrolyte batteries is the risk of mechanical damage to the packaging equipment leading to spillage or evaporation of the solvent. As a solvent, commonly flammable or toxic organic compounds (acetonitrile, N, N - dimethylformamide, dimethoxyethane, etc.) are frequently used [1]. In this paper, basic methods for measuring the properties of gel structure during polymerization, particularly relaxation times T_2 and diffusion coefficients, are introduced. We can obtain these parameters using the MR pulse sequences. We measured two sets of samples. To measure relaxation time T_2, the Hahn echo was used. To measure diffusion coefficients, the PFG-SE method (Pulsed Field Gradient Spin Echo) was used. All points of the FID signal are measured within the Hahn echo time. Consequently, it is necessary to approximate the FID signal by two exponential functions to obtain the T_2 time. Consequently, we assume the existence of two time constants T_2. For approximation, the genetic algorithm was chosen because it is a global optimization method. The algorithm is explained in the article.

2. Methods

Third-generation gel electrolytes combine three components: a) polymer networks of suitable composition, b) aprotic solvent, and c) organic salts to ensure conductivity (Li or Ni). For the experiments, gel electrolytes with conductivity based on sodium ions ^{+}Na were selected [2].

To measure the diffusion coefficients, the PFG-SE method as mentioned in the introduction was used. The PFG-SE sequence is shown in Figure 1 [2]. To measure relaxation time T_2, the Hahn echo as mentioned in the introduction was applied.

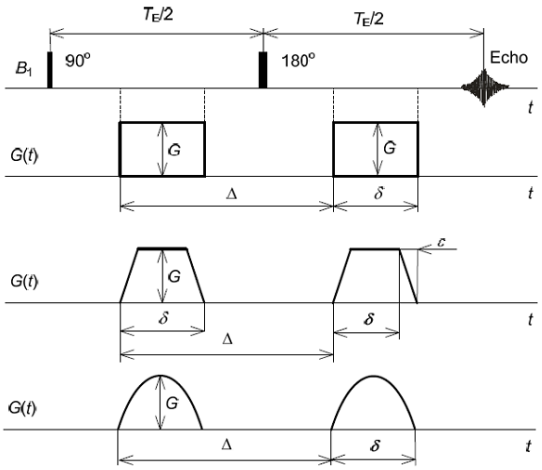

Fig. 1. The PFG-SE sequence and different shapes of diffusion gradients [2][3].

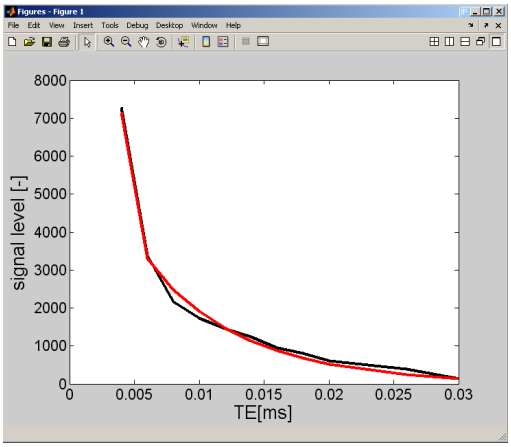

Fig. 2. Approximation of the measured data with two exponentials using a genetic algorithm. (^{23}Na nuclei, 1st set of gels, 1st samp., polymerization time = 0 min)

Genetic algorithm

All points of the FID signal are measured within the time of the Hahn echo course. Now we need to approximate these points by means of a suitable function. There exist a large number of optimization algorithms seeking the criterion function minimum. For example, the Trust-Region Methods for Nonlinear Minimization algorithm, which is contained in the MATLAB lsqcurvefit function, has proved to be effective. The advantage of this algorithm is its speed as well as the comparatively high success rate in the process of seeking the global minimum of our criterion function. From the user perspective, the disadvantage connected with the application of lsqcurvefit pertains mainly to the sophisticated setting of the optimization parameter and the necessity to have a MATLAB optimization toolbox [4]. Therefore, a genetic algorithm was used. An example of the approximation is shown in Figure 2. The main advantage is the ability to set the minimum and maximum values that we seek. However, the main disadvantage of this algorithm is the large computation time. The same genetic algorithm is used in [5]. All points of the FID signal are approximated by this function:

$$M(T_E) = M_{0a} \cdot e^{-\frac{T_E}{T_{2a}}} + M_{0b} \cdot e^{-\frac{T_E}{T_{2b}}}, \qquad (1)$$

where M_{0a}, M_{0b}, T_{2a}, T_{2b} are the searched values. The characteristics of the genetic algorithm are described in great detail in [5].

3. Experiment

The experiment was carried out on the NMR tomograph (4.7T/75mm) at the Institute of Scientific Instruments in Brno. The resonant frequency of ^{1}H nuclei is 200 MHz, and in ^{23}Na it is 51 MHz. The course of the experiment is consistent with the procedure described in [6]. The extension of procedure used to date consists in the fact that we measured *two* sets of gels based on the $NaClO_4$ inorganic salt. Furthermore, the measurement is extended to the measurement of diffusion. In the following table (Table 1) we can see individual composition

of the gels. $NaClO_4$ in PC (propylene) make a liquid electrolyte. After mixing with MMA (methyl methacrylic acid, 99%), EDMA (networking factor) and BEE (UV polymerization Initiator), gel electrolyte is gradually created by UV radiation (total time of polymerization for several hours)[6].

Table 1. 1st & 2nd set of measured samples

	1st samp.	2nd samp.	3rd samp.	4th samp.	5th samp.	1st samp.	2nd samp.	3rd samp.	4th samp.	5th samp.
	1st set of gels					2nd set of gels				
total volume of gel – V[ml]	12	12	12	12	12	6	6	6	6	6
PC [ml]	4,4	4,292	4,184	4,076	11,41	2,2	2,146	2,092	2,038	5,705
$NaClO_4$ [g]	0	0,270	0,538	0,808	1,470	0	0,135	0,269	0,404	0,735
MMA [ml]	7,657	7,657	7,657	7,657	-	3,8285	3,8285	3,8285	3,8285	-
EDMA [µl]	43	43	43	43	-	21,5	21,5	21,5	21,5	-
BEE [g]	0,17	0,17	0,17	0,17	-	0,085	0,085	0,085	0,085	-

4. Results

In the first set (Table 1) we are interested in T_2 relaxation of ^1H and ^{23}Na nuclei. In Figure 3 we can see the progress of relaxation T_{2a} and T_{2b} for ^1H nuclei. The progress for ^{23}Na nuclei is shown in Figure 4. Figure 5 observes the progress of diffusion in the second set of samples.

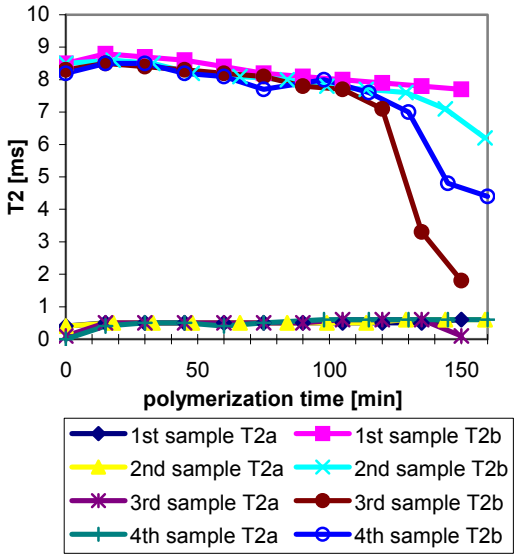

Fig. 3. T_2 relaxation during the polymerization for ^1H nuclei. 1st - 4th samples: 1st set of gels.

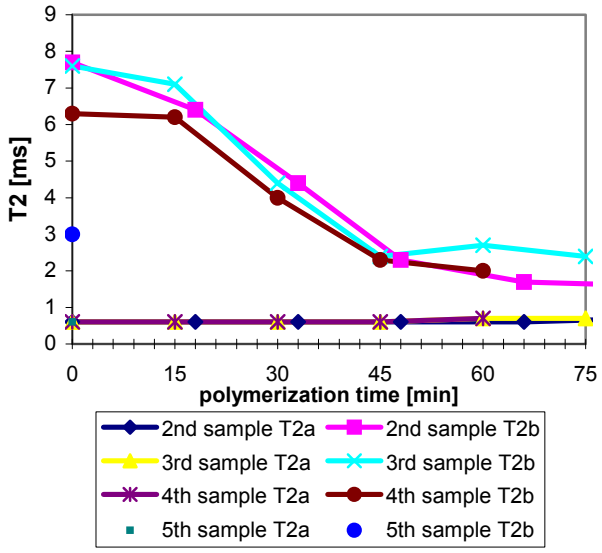

Fig. 4. T_2 relaxation during the polymerization for ^{23}Na nuclei. 1st - 4th samples: 1st set of gels.

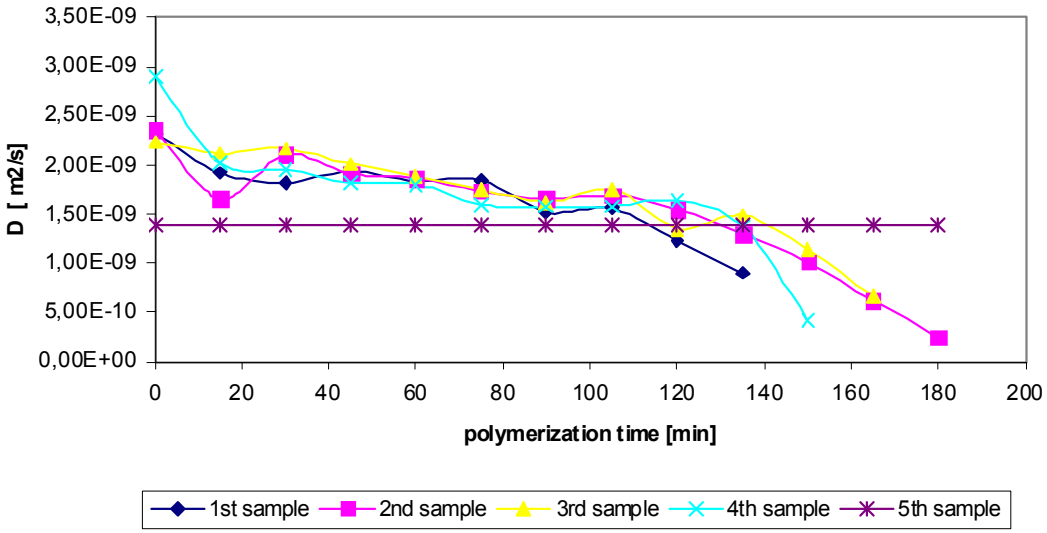

Fig. 5. The dependence of diffusion changes during polymerization for ^{1}H nuclei. 1st.- 5th. sample: 2nd set of gels.

5. Conclussion

The change in the structure of polymer gels during polymerization is characterized by T_2 relaxation. The decrease of relaxation time T_{2b} of gel with various concentrations is the same. These two aspects characterize the binding ^{23}Na nuclei in the gel. The second relaxation time T_{2a} is independent of the polymerization time. The measurement results will contribute to the study of changes in the structure of gel electrolytes.

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