

Investigation of the mechanism of sol-gel formation in the Sr(NO₃)₂/citric acid/ethylene glycol system by solution state ⁸⁷Sr nuclear magnetic resonance spectroscopy

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The polymerization mechanism of a modified Pechini process was investigated by ⁸⁷Sr nuclear magnetic resonance spectroscopy for the mixed solution of strontium nitrate, citric acid, and ethylene glycol. The *C*-ratio (the ratio of citric acid to metal ions in the polymer complex) is suggested to have a strong influence on the quality of the derived film. An analysis of the chemical shift variation, as a function of *C*-ratio, indicates the presence in the solution of two species: solvated strontium ions and strontium ions bound to the polymer complex, with a stoichiometry of 1:7. A polymeric precursor model based on this stoichiometry is proposed. Through a relaxation rate study of the strontium sites, it was found that the polymerization mechanism is predominantly bimolecular within the concentration region being studied. The equilibrium rate constant for the polymerization was calculated to be 10⁴ s⁻¹. A kinetic study of the fast cation exchange between the two identified strontium sites indicates that the inhomogeneity of the polymeric network leads to film cracking during pyrolysis.

I. INTRODUCTION

Over the past two decades, ionic and mixed-conducting ceramics have attracted much attention due to their increasing use in solid-state ionic or electrochemical devices or systems, such as batteries,¹ fuel cells,² gas sensors,^{3,4} chromatography detectors,⁵ and other applications. The material must be dense and uniform with a well-controlled stoichiometry to achieve high electrical conductivity⁶ and sufficiently thin to minimize resistive loss.⁷ However, the membranes must be deposited on porous electrodes in order to be accessible to gases and ions, which participate in electrode reactions on electrode surfaces.

The Pechini process, a solution mixing process based upon an aqueous polyalcohol–citric acid system in which a wide range of metal salts are soluble,⁸ has been used widely in the preparation of complex ceramic powders and thin films on dense substrates.^{7–10} Further, it has been demonstrated¹¹ that, with proper modification, the Pechini process can be used to prepare crack-free, uniform, and dense thin-film coatings on both dense and porous substrates. In the latter work, the effect of several parameters on the quality of the derived thin films of LSCF (La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3–δ}) on porous Al₂O₃ substrates was studied. The most important processing parameter identified was the *C*-ratio (the ratio of complexation/polymerization agent–citric acid to total metal ions). It was observed that a solution with either a small ratio (e.g., *C* ≤ 1.0) or a large ratio (e.g., *C* ≥ 4.0) would lead to cracking in the derived films in contrast to an optimal *C*-ratio of 3.5; the quality of the derived films, however, was much less sensitive to the ratio of citric acid to ethylene glycol. To date, these observations have

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not been explained fully because of the lack of understanding of the polymerization mechanism; thus, a polymeric structure model needs to be developed.

It is believed that the quantity of the derived films is determined by the microstructural evolution of the polymeric network and the mechanism of the polymerization, and strontium ions are involved in the polymerization process.¹¹ Teraoka *et al.*² concluded that the oxygen permeability of LSCF membranes increases with Sr content. Thus, variations in strontium concentration and C-ratio provide an opportunity to examine the polymerization mechanism. ⁸⁷Sr nuclear magnetic resonance spectroscopy (NMR) may provide some insight into the structure of the sol-gel polymeric network.

Quadrupolar NMR is a local probe of molecular dynamics. Line shape, relaxation, or chemical measurements can usually be obtained from the NMR signals of nuclei at particular chemical sites, even in quite complex molecules. It is possible therefore to probe, to identify, and to compare molecular motions at various locations. The qualitative interpretation of NMR data related to molecular dynamics typically involves utilization of models for the kinetic study. To date, NMR has been used to characterize the mechanism by which small organic complexing agents exchange host metal cation for Na⁺ ($I = 3/2$),^{12–15} K⁺ ($I = 3/2$),^{13–16} Cs⁺ ($I = 7/2$),^{14,17,18} and others. In these studies, the variation of chemical shift as a function of the ratio of the complexing agent to the metal ions has been used to determine the complexation number. In the case of operation in the region of the extreme narrow limit ($\omega_0\tau_c \ll 1$), longitudinal and transverse relaxation rates have been related to the pseudo-first-order rate constant of the two-site exchange mechanism.^{13–15,17,18} Unimolecular complexation/decomplexation and bimolecular cation exchanges have been the two most considered mechanisms; however,

little success has been achieved for the complexation process involving species other than mono- and bidentate ligands.

The only NMR-active isotope of strontium, ⁸⁷Sr, has a spin number of 9/2, a natural abundance of 7.02%, and a quadrupole moment of $0.36 \times 10^{-24} \text{ cm}^2$.¹⁹ These characteristics are unfavorable for observation. However, the ⁸⁷Sr NMR signal was detected as early as 1959 with a 1 T instrument by Jeffries and Sogo.²⁰ The current ready availability of more advanced NMR instruments and better computer programs make ⁸⁷Sr NMR more accessible.

In this study, the dynamic ⁸⁷Sr NMR behavior of ligand-derived solution coating by sol-gel have been explored. To simplify the component of the LSCF thin films, only strontium nitrate was added into the mixture of citric acid and ethylene glycol. Chemical shift and relaxation time measurements were carried out on the sol-gel solutions with different C-ratios. The polymerization mechanism was examined. A sol-gel structural model was developed, and the impact of the processing parameters on the quality of the derived film has been suggested.

II. EXPERIMENTAL PROCEDURE

A. Preparation of sol-gel solutions

Strontium nitrate, citric acid, and ethylene glycol (each ACS reagent grade) were obtained from Aldrich (Milwaukee, WI) and used as received. The procedure for the preparation of the sol-gel solution was as described elsewhere.¹¹ First, 2.1163 mg of Sr(NO₃)₂ was introduced into 4 ml of distilled water under stirring, and when the strontium precursor was completely dissolved in the solution, controlled amounts of citric acid and ethylene glycol were added (the amount of citric acid and ethylene glycol determines the ratio of citric acid to metal

TABLE I. Examples of sol-gel solutions.

[Citric acid]/[Sr ²⁺]	Sr(NO ₃) ₂ (g)	Citric acid (g)	Ethylene glycol (ml)	[Ethylene glycol]/ [citric acid]
0.2	2.116	0.384	0.32	2.9
0.5	2.116	0.960	0.84	3.0
1.0	2.116	1.920	1.62	2.9
2.0	2.116	3.840	3.12	2.8
2.5	2.116	4.800	3.76	2.7
3.0	2.116	5.760	4.02	2.4
3.5	2.116	6.720	4.29	2.2
4.0	2.116	7.680	4.69	2.1
4.5	2.116	8.640	5.02	2.0
5.0	2.116	9.600	5.58	2.0
5.5	2.116	10.56	6.75	2.2
6.0	2.116	11.52	7.03	2.1
6.5	2.116	12.48	7.25	2.0
7.0	2.116	13.44	10.93	2.8
7.5	2.116	14.40	9.62	2.3
8.0	2.116	15.36	9.37	2.1
8.5	2.116	16.32	10.43	2.2

strontium ions and the ratio of citric acid to ethylene). The solution was heated at 80 °C for 30 min until it was viscous. The examples of the composition of a few sol-gel solutions are summarized in Table I.

The sol solutions were diluted with distilled water to the same concentration of $[\text{Sr}^{2+}]$ (0.313 M), and a few drops of D_2O were put into each 10-mm NMR tube prior to execution of the NMR experiment. All spectra were recorded within 24 h after the solutions were prepared.

B. Chemical shift measurement

^{87}Sr NMR measurements were performed using a wide-bore Bruker AMX-400 (Billerica, MA) spectrometer operating at a resonance frequency of 17.34 MHz. ^{87}Sr NMR spectra typically were acquired with the following parameters: 70- μs ($\pi/2$) pulse length; sweep width of 71428 Hz; acquisition time of 28.7 ms (for broad signals, such as those of the samples) or 57.4 ms (for narrow signals, such as those of the standard); repetition time of 40 ms. All data were zero-filled prior to processing, and an exponential multiplication, resulting in a line broadening of 100 Hz, was applied to different sets of experiments. ^{87}Sr NMR chemical shifts were measured with respect to 1 M $\text{Sr}(\text{NO}_3)_2$ solution in D_2O . A D_2O lock was used for all experiments. Sample temperature was determined by a thermocouple preinstalled in the NMR instrument. Sample temperatures were determined independently to be reliable to ± 0.5 °C. The temperature range examined was 296 to 353 K.

C. Relaxation time measurement

Longitudinal relaxation time (T_1) measurements were done at 17.34 MHz (Bruker AMX, 400 MHz), using the inversion-recovery $180^\circ-\tau-90^\circ$ pulse sequence; 90° pulse widths were 70 μs (17.34 MHz). Repetition time (D_1) was 40 ms. T_1 was obtained from a nonlinear regression analysis (by computer).

Relaxation rates (R_2) were obtained from the line-widths at half amplitude ($\Delta\nu_{1/2}$) of the absorption spectra, utilizing the relationship $R_2 = \pi\Delta\nu_{1/2}$.

D. Data processing

Kinetic parameters were calculated by fitting rate data at various temperatures to appropriate equations, using EXCEL on a Dell computer.

III. RESULTS AND DISCUSSION

A. Characterization of the complexation number

The complexation number has been determined to be one of the most important processing parameters in the modified Pechini process.¹¹ Although this point was not key to the initial disclosure of the technique,⁸ quantitative determination of the complexation number is essential for sol-gel structure determination, which is one key point to further exploration of the polymerization/

complexation mechanism. The ^{87}Sr NMR chemical shift variation as a function of C -ratio is plotted in Fig. 1. The observation of a sharp cutoff at the C -ratio = 7.0 is indicative of complexation of the strontium cation by citric acid to create a 1:7 complex. The linear relationship of the curve in the range of C -ratio = 0.2–8.5 suggests the coexistence of only two species:¹⁵ solvated and 1:7 complexed strontium. The system, therefore, can be regarded as a two-site system. The line shapes of the spectra obtained at 17.34 MHz were Lorentzian for the concentration range under examination. Additionally, one sharp signal was observed for each solution, as opposed to two. This further confirms that exchange between the two strontium sites is fast, since the exchange rate has a substantial influence on the band shape.^{21,22} For example, if there is a chemical shift difference of 1.00 ppm at 100 MHz for two sites, the frequency difference is 100 Hz. Thus, in an exchanging system, only one signal (corresponding to both sites) is observed, if the exchange rate is substantially faster than 100 Hz.

B. Relaxation studies

A perturbed nuclear spin system relaxes to its equilibrium state or steady state by first-order processes characterized by two relaxation times: T_1 , the spin–lattice, or longitudinal time; T_2 , the spin–spin, or transverse time. Relaxation occurs only if there is some specific interaction between the nucleus and its environment which results in energy exchange.

On the basis of the chemical shift measurement, the longitudinal relaxation rate should have a similar behavior in the sol-gel system under exploration. The relaxation rate observed is the average of the characteristic relaxation rates of solvated and complexed species. Thus, a linear decrease of T_1^{-1} , as a function of C -ratio, in the range 0–7.0, as well as the occurrence of a plateau at values in excess of 7.0, would be anticipated, as is observed in Fig. 2. The measured transverse relaxation rate

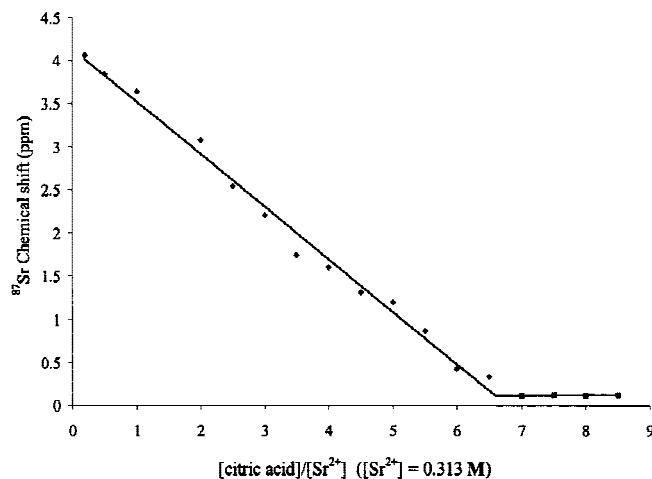


FIG. 1. ^{87}Sr NMR chemical shift as a function of $[\text{citric acid}]/[\text{Sr}^{2+}]$.

behavior is different from T_1^{-1} (Fig. 2) and chemical shifts (Fig. 1). $T_{2,\text{obsd}}^{-1}$ (directly from the linewidth of the Lorentzian signal), as a function of C -ratio, is shown in Fig. 3. A maximum is observed for a C -ratio of approximately 6.0. It readily is apparent that the measured relaxation rate behavior is different from T_1^{-1} and chemical shifts. This indicates that T_2^{-1} and T_1^{-1} are not in phase, which suggests that some exchange-broadening contribution to T_2^{-1} might be present. This notion was examined and further tested in a variable-temperature study.

The variation of $\ln(T_1^{-1})$ and $\ln(T_2^{-1})$ as a function of T^{-1} (the inverse of the temperature), is shown in Fig. 4 for $[\text{citric acid}]/[\text{Sr}^{2+}] = 3.5$. The larger slope in the case of $\ln(T_2^{-1})$, when compared to that of $\ln(T_1^{-1})$, confirms the (moderately) rapid exchange between the two strontium sites.²³ At this point, it may be suggested that chemical exchange broadening is another relaxation

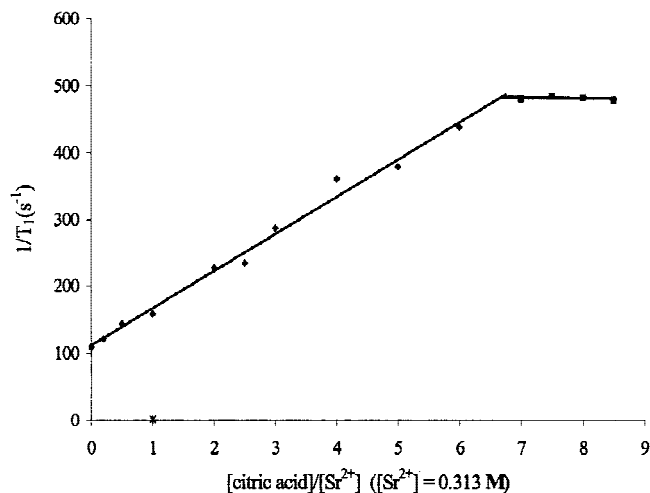


FIG. 2. ⁸⁷Sr NMR longitudinal relaxation rates as a function of $[\text{citric acid}]/[\text{Sr}^{2+}]$.

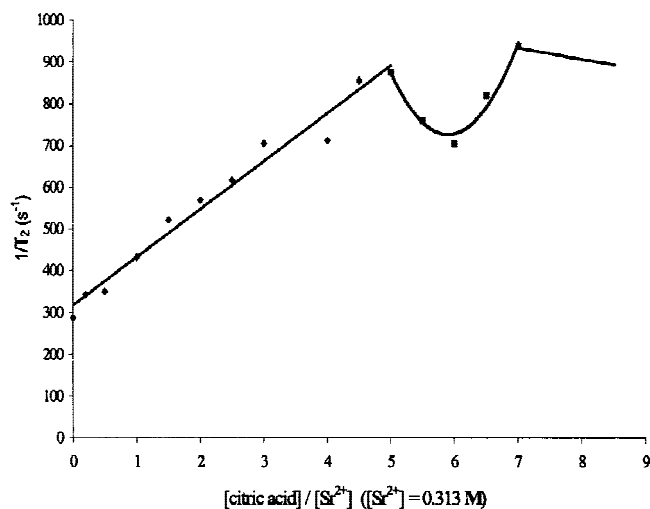


FIG. 3. ⁸⁷Sr NMR transverse relaxation rates as a function of $[\text{citric acid}]/[\text{Sr}^{2+}]$.

mechanism (in addition to the quadrupolar effect) which impacts the transverse relaxation rates.²⁴ Therefore, the observed transverse relaxation rates contain quadrupolar, chemical exchange, and inhomogeneity contributions as shown in Eq. (1).¹⁵

$$T_{2,\text{obsd}}^{-1} = T_{2,\text{inh}}^{-1} + T_{2,\text{ex}}^{-1} + T_{2,\text{q}}^{-1} \quad (1)$$

In the extremely narrow limits, $T_{2,\text{obsd}}^{-1} = T_{1,\text{q}}^{-1} = T_{2,\text{q}}^{-1}$, and $T_{2,\text{inh}}^{-1}$ is given by $T_{2,\text{obsd}}^{-1} - T_{1,\text{obsd}}^{-1}$ in the case of $[\text{citric acid}]/[\text{Sr}^{2+}] = 0$, where the exchange contribution is negligible.¹³ A plot of $T_{2,\text{ex}}^{-1} = T_{2,\text{obsd}}^{-1} - T_{2,\text{q}}^{-1} - T_{2,\text{inh}}^{-1}$ as a function of C -ratio is shown in Fig. 5. The sum of k_A and k_B is about 230 ± 40 Hz for most of the sol-gels (Table II). For $[\text{citric acid}]/[\text{Sr}^{2+}] = 0.2$ and 0.5 , the NMR linewidth was broad, and $k_A + k_B$ could not be determined accurately. The data are fit by a parabolic model, as discussed below.

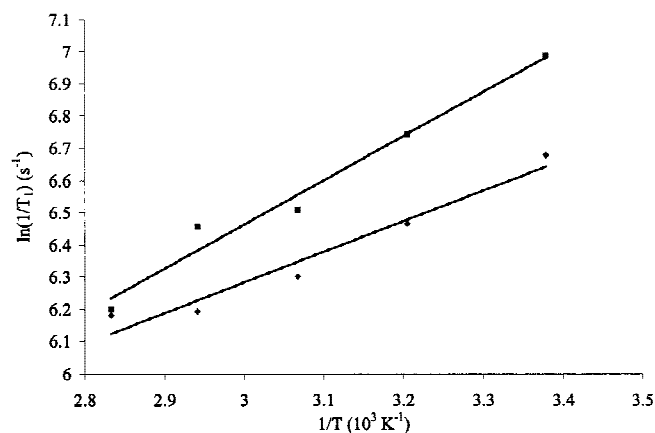


FIG. 4. ⁸⁷Sr NMR transverse (top) and longitudinal (bottom) relaxation rates as a function of inverse temperature, for $[\text{citric acid}]/[\text{Sr}^{2+}] = 3.5$.

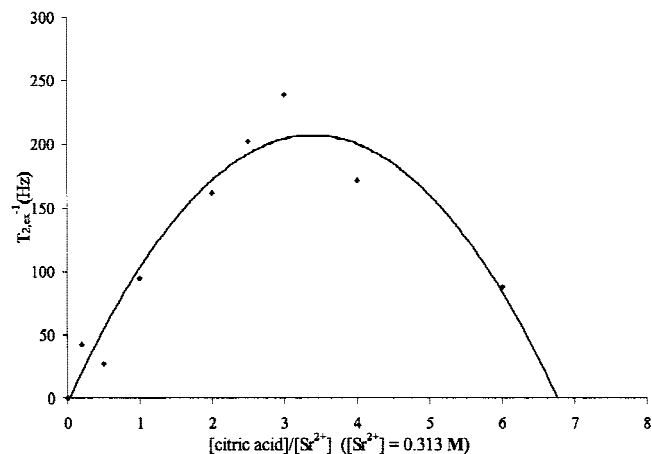


FIG. 5. Chemical exchange contribution to the ⁸⁷Sr NMR transverse relaxation rate for the sol-gel network as a function of $[\text{citric acid}]/[\text{Sr}^{2+}]$.

TABLE II. Chemical exchange contribution to the ⁸⁷Sr transverse relaxation rate of the sol-gel.

[Citric acid]/[Sr ²⁺]	$T_{1,\text{obsd}}^{-1}$ (Hz)	$T_{2,\text{obsd}}^{-1}$ (Hz)	$T_{2,\text{ex}}^{-1}$ (s ⁻¹)	$k_a + k_b$ (Hz)
0	287.61	108.64	0	0
0.2	342.4	121.05	42.38	121.17
0.5	349.25	143.28	26.99	454.67
1	431.44	157.75	94.7	239.23
2	568.41	227.53	161.9	233.22
2.5	616.32	234.58	202.76	209.50
3	705.35	287.11	239.26	189.38
4	712.2	361.53	171.69	263.91
6	705.35	438.79	87.58	258.68

C. Kinetic studies

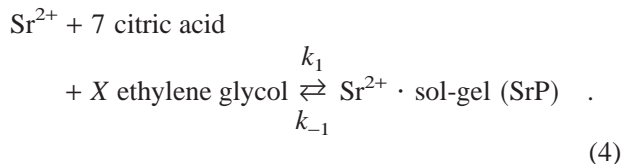
T_2 is related to the chemical shift and rate constant on the basis of the chemical shift expression derived from the Bloch equation.²⁵ This provides the basis for calculation of the exchange rate constant between two uncoupled sites by the determination of both T_1 and T_2 .^{12,26} ⁸⁷Sr NMR relaxation is suitable for studying the polymerization mechanism in this case, since the exchange rate between the two strontium sites is rapid.

For a two uncoupled site case [Eq. (2)], $T_{2,\text{ex}}^{-1}$ can be expressed by Eq. (3).^{19,26}



$$T_{2,\text{ex}}^{-1} = 4p_A p_B \pi^2 (\nu_A - \nu_B)^2 (k_A + k_B)^{-1}, \quad (3)$$

where p_A and p_B are the molar fraction of site A and B, ν_A and ν_B are the respective chemical shifts of these two sites in hertz, and k_A and k_B represent the inverse of the cation residence times in sites A and B, respectively. Equation (4) represents the sol-gel complexation/polymerization chemistry for strontium system studied here.



The concentration of the complexed Sr²⁺ [SrP] can be expressed in Eq. (5):

$$[\text{SrP}] = \frac{1}{7}[\text{complexed citric acid}] = \frac{1}{7}([\text{citric acid}]_T - [\text{citric acid}]) \quad (5)$$

Since the C -ratio = [citric acid]_T/[Sr²⁺]_T, therefore, [citric acid]_T = C -ratio · [Sr²⁺]_T, and, by insertion of this term into Eq. (5), the following equation may be obtained:

$$[\text{SrP}] = \frac{1}{7}(C\text{-ratio} \cdot [\text{Sr}^{2+}]_T - [\text{citric acid}]) \quad (6)$$

At equilibrium, the [citric acid] term may be neglected as a constant, and Eq. (6) simplifies to [SrP] = $\frac{1}{7}C$ -ratio · [Sr²⁺]_T. The molar fraction of the complexed Sr²⁺ can be expressed as $p_{\text{SrP}} = [\text{SrP}]/[\text{Sr}^{2+}]_T = \frac{1}{7}C$ -ratio. The parabolic curve in Fig. 5, therefore, has a maximum value for $p_{\text{SrP}} = 3.5/7 = 0.5$. This is in good agreement with Eq. (3), since the maximum value of the product $p_A p_B$ corresponds to $p_A = p_B = 0.5$. More importantly, the sum of ($k_A + k_B$) is independent of C -ratio (Table I), thus providing the underpinning for the examination of the sol-gel complexation/polymerization mechanism.

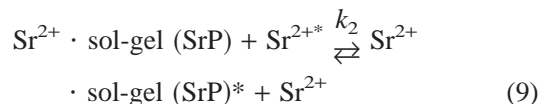
It is reported^{15,23} that unimolecular complexation and bimolecular cation exchange are the two most considered mechanisms for the kinetic studies of complexation. The unimolecular mechanism is represented by Eq. (4), which leads to Eq. (7). This further leads to Eq. (8), due to the high value of the complexation constant.

$$k_A + k_B = k_1[\text{citric acid}]^7[\text{ethylene glycol}]^X + k_{-1} \quad (7)$$

$$k_A + k_B = k_{-1}(1 - \frac{1}{7}([\text{citric acid}]/[\text{Sr}^{2+}]_T))^{-1} \quad (8)$$

In Eq. (8), k_A and k_B represent the pseudo-first-order exchange rate constant between site A (the free strontium ion site) and B (the complexed strontium site). The equation shows the dependence of $k_A + k_B$ on C -ratio, so the unimolecular complexation mechanism can be ruled out.

A bimolecular cation exchange [Eq. (9)] would lead to $k_A + k_B = k_2[\text{Sr}^{2+}]$, where the sum of $k_A + k_B$ is independent of [citric acid]/[Sr²⁺].



To test the possibility of the bimolecular mechanism, the relaxation times of several solutions ([citric acid]/[Sr²⁺] = 3.5) with different concentrations were measured. A linear relationship between $k_A + k_B$ and [Sr²⁺]_T [the initial concentration of Sr(NO₃)₂] is observed in Fig. 6, with a slope of $k_2 = 0.74 \times 10^3 \text{ s}^{-1}$. This

confirms that, for the concentration region of $[\text{Sr}^{2+}]$ being studied (0.313–0.01 M), a bimolecular mechanism dominates, and the exchange between the two strontium sites is rapid.

D. Parameters for the modified Pechini process

In the Pechini process, selection and optimization of processing parameters are critical to the preparation of ceramic films with desired microstructures and properties. Many efforts have been devoted to the parameter selection to obtain the best film quality.^{7,9,10,11} Among all the parameters studied, the ratio of the chelating agent (e.g., citric acid) to the metal ions, $[\text{citric acid}]/[\text{Sr}^{2+}]$, appeared to be the most important.¹¹ However, the influence of those parameters on the quality of the derived film cannot be explained without an understanding of the structural evolution during processing. The kinetic study of the complexation/polymerization mechanism offers a simple explanation for the importance of $[\text{citric acid}]/[\text{Sr}^{2+}]$.

As stated earlier, the cation exchange between solvated strontium and complexed strontium is fast ($k_2 = 0.74 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) and the complexation number of the strontium present in the sol-gel is 7 (to citric acid). Therefore, $[\text{citric acid}]/[\text{Sr}^{2+}]$ must be (approximately) 3.5, to achieve the cation exchange equilibrium at $p_{\text{Sr}^{2+}} = p_{\text{SrP}} = 0.5$, assuming that neither of the strontium sites is in excess, and the sol-gel network is homogeneous with respect to strontium ions. However, when $[\text{citric acid}]/[\text{Sr}^{2+}]$ is quite small (e.g., <1.0), there would be a large amount of excess $\text{Sr}(\text{NO}_3)_2$ remaining at equilibrium, which distributes among the sol-gel network, creating a migration of Sr^{2+} to the location with more H_2O during pyrolysis. This further leads to an inhomogeneity in the distribution of the $[\text{Sr}^{2+}]$ in the dried film and, ultimately, initiates cracking. In contrast, for sol-gel solutions with large C -ratios (e.g., >4.0), the removal of the organic compounds during pyrolysis leaves substantial pores in the polymer,²⁸ which were filled initially by the small organic molecules in the gel

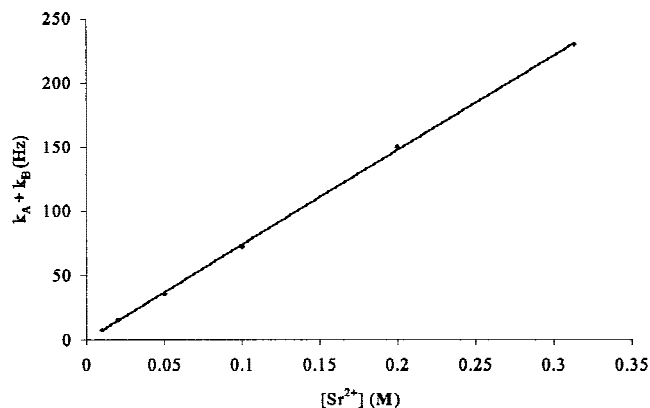


FIG. 6. Sum of $k_A + k_B$ as a function of the initial strontium ion concentration at $[\text{citric acid}]/[\text{Sr}^{2+}] = 3.5$.

solution. These pores cannot be eliminated during firing, due to the low packing density of metal ions, and lead to cracking.

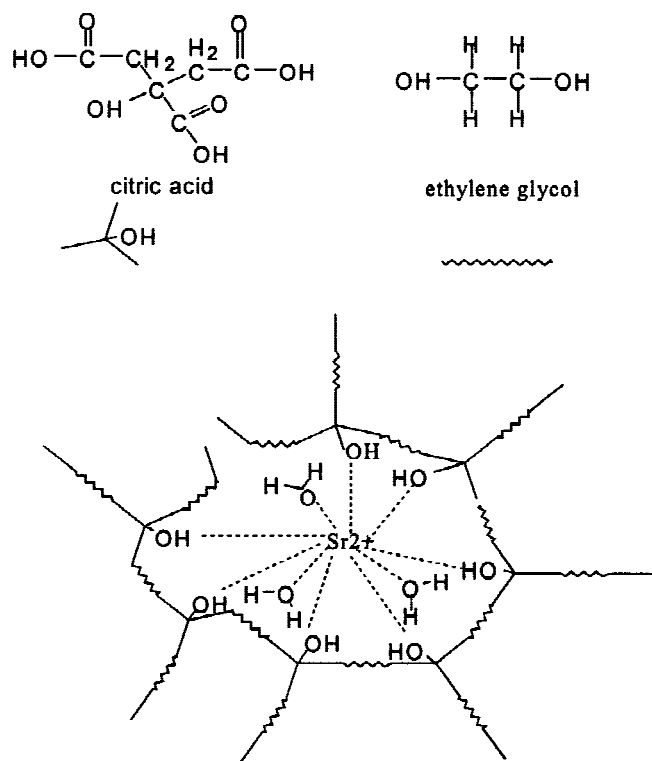
It is known that the drying and film formation mechanism in the (modified) Pechini process is to obtain a sol-gel precursor comprising randomly coiled macromolecular chains throughout which the metal cations are uniformly distributed at an atomic level.¹¹ The ceramic film will not form until the organic network is removed during the ignition of the polymeric matter. Accordingly, film cracking usually occurs during the pyrolysis of the film, rather than the drying of the film.¹¹ Therefore, the purity of the polymer precursor is highly critical to the ultimate success in film formation. Thus, the homogeneity of the sol-gel network is among the most important factors in the Pechini process. For this present study, $[\text{citric acid}]/[\text{Sr}^{2+}]$ is the parameter controlling homogeneity.

This conclusion is consistent with the thermal analysis result of the LSCF film in a previous study.¹¹ The sol-gel with $[\text{citric acid}]/[\text{Sr}^{2+}] = 1$ or 3 showed type II characteristics²⁷ for the pyrolysis. In other words, the decomposition of both precursors follows the type II pyrolysis reaction. This confirms that the polymer precursor structures are the same for different ratios of $[\text{citric acid}]/[\text{Sr}^{2+}]$. It was also found that the only difference between the two gels ($[\text{citric acid}]/[\text{Sr}^{2+}] = 1$ and 3) was that the pyrolysis of the first gel started and completed at lower temperatures than that of the latter gel with $[\text{citric acid}]/[\text{Sr}^{2+}] = 3$. According to the kinetic study result, the sol-gel precursors have the same structure; however, there are more organic components to be removed in the latter gel than in the first gel. The organic agents used are high boiling point organic compounds (e.g., ethylene glycol, b.p. 196–198 °C); therefore, it is expected that the latter gel should have a higher pyrolysis temperature.¹¹

E. Polymer precursor model

It is clear from the present data that $[\text{citric acid}]/[\text{Sr}^{2+}]$ does not have an effect on the structure of the sol-gel precursor, although it was thought previously that sol-gels having different ratios of $[\text{citric acid}]$ to $[\text{Sr}^{2+}]$ might possess a different structure. It was observed that $[\text{citric acid}]/[\text{Sr}^{2+}]$ influenced the quality of derived films because it plays an important role in the control of the homogeneity of the sol-gel network. On the basis of the complexation number of the strontium ion (to citric acid) by ^{87}Sr NMR analysis, a quantitative polymer precursor model (Scheme I) is suggested.

On the basis of this model, the ratio of ethylene glycol to citric acid ($[\text{EG}]/[\text{CA}]$) can be expressed by $(2n + 1)/n$, where n is the number of citric acid sites in the sol-gel network. Therefore, the sol-gel precursor will be homo-



SCHEME I. Sol-gel polymer structure model.

geneous, provided that this ratio falls into the region of 2–3. Thus the ratio of [EG]/[CA] is less critical to the film quality, as observed in a previous study.¹¹

The reaction involved in the modified Pechini process can be described as follows. When the mixture of Sr(NO₃)₂, citric acid, and ethylene glycol is heated, polyesterification occurs between the carboxylic acid groups of citric acid and the hydroxyl groups of ethylene glycol to form the sol-gel backbone. Therefore, only the hydroxyl groups in citric acid are available to coordinate with strontium ions. The coordination number of strontium can be accommodated by H₂O as shown in Scheme I. Thus, strontium ions are very stable in the sol-gel network and remain homogeneously distributed.

IV. SUMMARY

One promising material for utilization in solid state ionic or electrochemical applications, (La,Sr)(Co,Fe)O_x, often is prepared as a thin film coating on dense substrates by sol-gel techniques. In previous explorations, the structural quality of these coatings was observed to depend heavily on the molar ratio of citric acid to metal ion present in solution. A model system containing only strontium has been examined in detail. The sol-gel polymeric network created by the condensation of ethylene glycol and citric acid has been probed, and a model is suggested for the binding environment present around Sr⁺², based on ⁸⁷Sr NMR spectroscopy.

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