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^{23}Na NMR Studies Of Na$_x$Co$_2$ Cathode Materials

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^{23}Na NMR STUDIES OF Na$_x$CoO$_2$ CATHODE MATERIALS

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Abstract

Two samples of oxidized sodium cobalt oxide, Na$_x$CoO$_2$, where x = 0.3 and 0.7, have been studied by variable-temperature wide-line ^{23}Na NMR. All spectra exhibit a substantially paramagnetic-shifted response characterized by 2nd-order quadrupole broadening and a diamagnetic-shifted weaker response. The paramagnetic shifts are attributed to spins localized on cobalt atoms. The 2nd-order quadrupolar splitting is resolved for x = 0.7; whereas the lineshapes obtained for x = 0.3 do not show the resolution and indicate a more symmetric sodium environment and/or a greater degree of ion mobility. Lineshapes for the two compositions behave somewhat differently as the temperature is changed, although both samples exhibit gradual line-narrowing over the entire range (-150 to 100°C). Spin-lattice relaxation time measurements reflect the presence of inequivalent sodium environments, with one distribution of sodium environments characterized by long relaxation times (10 ms - 200 ms) and another set of environments characterized by much shorter times (< 500 µs).

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Introduction

There are several alkali-transition metal oxides currently being studied and developed for use as electrodes in rechargeable batteries. Lithium based batteries are the most popular due to their relatively high theoretical energy densities; however, upon consideration of manufacturing costs, sodium based batteries can have an advantage. Until recently, it has been difficult to find a sodium cell which exhibits the desirable characteristics that lithium based batteries possess. Therefore, it is of interest, in order to obtain practical sodium batteries, to improve several facets of sodium cell technology.[1]

The choice of a suitable cathode material is crucial to the performance of a sodium cell. Not only must the material intercalate/deintercalate sodium ions to a large degree, but it must also show good reversibility. Na_xCoO_2 is one candidate that exhibits these desirable properties. Furthermore, it has been shown that cells utilizing Na_xCoO_2 as cathodes are characterized by theoretical energy densities and reversibility characteristics that are compositionally dependent[2]. In particular, cathode performance is optimized when x is near 0.7.

Previous charge and discharge studies of rechargeable Na/Na_xCoO_2 and $Na_{15}Pb_4/Na_xCoO_2$ cells, using polyethylene oxide as an electrolyte, have shown that these cells rival comparable lithium cells in performance, yet can be fabricated at a reduced cost[3]. For these cells, the amounts of sodium, x, which can be intercalated or deintercalated is reflected in the limiting compositions of the charging/discharging cycle, e.g. the compositional parameter x ranges between 0.3 and 0.9 ($\Delta x = 0.5$ to 0.6).

Typically, the electrochemical behavior of cells utilizing Na_xCoO_2 as cathodes reveal many "steps", which reflect the presence of two-phase domains within the cathode material. Distinct structural phases can appear for Na_xCoO_2 as the cell charges or discharges, and the structural differences between phases is due to the distribution of sodium ions which are interspersed between layers of CoO_6 octahedra and the orientation of the correponding CoO_2 sheets. Two types of sodium environments are found: trigonal prismatic (P) and octahedral (O). There are variations in the phases depending upon the number and arrangement of CoO_2 sheets; the phase type depends upon the composition of the starting material (prior to cycling) and the

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amount of sodium between the CoO_2 sheets. Reversible intercalation/deintercalation of sodium has been observed over the composition range of approximately $0.3 \leq x \leq 0.9$ where generally only one of the possible P phase structures, denoted as P2, is maintained.[2] Small structural distortions do occur depending upon the amount and distribution of sodium ions. In order to obtain quantitative information about the sodium cation distributions, ^{23}Na NMR experiments were conducted upon two samples of Na_xCoO_2 corresponding to x = 0.3 and 0.7.

Experimental

Sample Preparation

$Na_{0.7}CoO_2$ bronzes were fabricated by a glycine-nitrate combustion synthesis method. Sodium nitrate and cobalt nitrate, in the appropriate stoichiometric ratio, were dissolved in water followed by an equimolar amount of glycine. The solution was heated unitl spontaneous combustion occurred. The resultant blue-black powder was calcined at 750° C in air for 4 hours to remove residual organic impurities. X-ray powder diffraction (Siemens diffractometer) and elemental analysis (atomic absorption, performed by the U.C. Berkeley Microanalytical Laboratory) was used to confirm the structure and composition. The oxidized form, $Na_{0.3}CoO_2$, was prepared by a "chimie douce" technique by adding $Na_{0.7}CoO_2$ to an aqueous solution (buffered to pH = 10) containing a stoichiometric amount of sodium persulfate and stirring 12 hours. The powder was filtered and washed well with deionized water, then dried in vacuo for 24 hours. XRD and elemental analysis were used to confirm that oxidation to $Na_{0.3}CoO_2$ had taken place without structural changes. Elemental analysis gave a formula of $Na_{0.26}CoO_{2.26}$. The somewhat high oxygen content suggests that some water may be present.

^{23}Na NMR Measurements

NMR measurements were performed on polycrystalline samples at 79.62 MHz using a Chemagnetics CMX 300 spectrometer and at 54.39 MHz on a Novex broadband spectrometer with a LeCroy 9400A digital oscilloscope. Employing a single $\pi/2$ pulse (2.4 μs) with phase-cycled detection, good signal-to-noise was obtained after averaging about 500 to 1000 free induction decay transients. Sample volumes were roughly 0.5 cc. Lineshapes were obtained

throughout the temperature range of -150° to 100° C. Spin-lattice relaxation times (T_1) were extracted from recovery profiles of the inversion recovery pulse sequence. In general, recoveries were non-exponential, due to the distributions of relaxation times.

Results and Discussion

Measurements for $Na_{0.7}CoO_2$

Room temperature [23]Na spectra gathered for $Na_{0.7}CoO_2$ at 79.62 MHz reveal two components separated by isotropic chemical shifts (Fig. 1). The strong response on the higher frequency side (paramagnetically shifted) has a width of roughly 30 kHz and displays resolvable divergences indicative of 2nd-order quadrupolar broadening of the -½↔½ transition. Satellite responses were not observed. Due to motional averaging and distributions amongst sodium sites, accompanying shoulders of the powder pattern are not resolvable. Reasonable one site simulations of the lineshape can be performed yielding quadrupolar parameters of $\eta = 0.2$ and $e^2qQ/h = 3.60$ MHz, where η is the asymmetry parameter of the electric field gradient and e^2qQ/h is the quadrupole coupling constant. It is important to note that these values are reflective of partially motionally averaged conditions, as explained later in the context of the variable temperature results. Verification of quadrupole parameters was performed by gathering spectra at 54.39 MHz (Fig. 2); thereby confirming the expected inverse frequency dependence of the 2nd-order splitting. Deviations between lineshapes and simulations are observed which reflect a combination of chemical shift anisotropy, structural distributions, nuclear dipole-dipole interactions and averaging effects due to atomic motions. The much less intense response on the lower frequency side of the spectrum (diamagnetically shifted) has a linewidth of about 15 kHz, and does not reveal resolvable quadrupolar features. Typically, this indicates a highly symmetric sodium environment.

[23]Na lineshapes were also obtained at various temperatures. Associated linewidths attained their smallest values for temperatures above 25° C. The lineshapes became broader with decreasing temperature and continued to broaden down to the lowest temperature attainable in this study (-150° C). For temperatures below -10° C, the 2nd-order quadrupolar features were irresolvable, presumably due to distributions in sodium sites and hetero- and homonuclear dipole

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broadening. Considering the nature of this system, it is reasonable to expect the influence of at least two types of broadening mechanisms: 1) motional effects - as the temperature is lowered, sodium structural environments become "frozen out" resulting in larger distributions of resonant frequencies and larger nuclear dipole broadening; 2) paramagnetic dipolar interactions - due to the natural temperature dependence of the paramagnetic suscept-ibility, broadening is enhanced at lower temperatures.

Spin-lattice relaxation times gathered for the intense 2nd-order quadrupolar broadened response were obtained by fitting magnetization recovery profiles with two-site exponential functions (with roughly 50:50 weighting). Most recovery profiles could not be interpreted by a single exponential. The slowly relaxing component typically gave T_1 values (10 ms - 20 ms) that were much longer than the more quickly relaxing component (< 500 μs). The T_1 results of the slowly relaxing component for the intense 2nd-order quadrupolar broadened response is given in Fig. 3. The T_1 results for the weaker response is also shown; typically these values are on the order of seconds. Fig. 4 shows the results of an inversion recovery experiment, illustrating the different recoveries for the strong and weak ^{23}Na NMR responses.

All T_1 profiles show increasing behavior with decreasing temperature; furthermore, no minima were found - they presumably reside above 100° C. These observations suggest that line narrowing with increasing temperature is primarily a motional effect. Additionally, the fact that complete motional narrowing is not observed in the high temperature spectra (i.e. liquid-like behavior), indicates that the 2nd-order quadrupolar broadened response is partially averaged, and that sodium ion motion is still constrained considerably.

Based on the line width and T_1 results, the less intense diamagnetically shifted response is attributed to a highly symmetric sodium site (e.g. cubic or octahedral) for the x = 0.7 sample. It broadens considerably at lower temperatures and the T_1 minimum is not observed. Provided the NMR responses account for all sodium atoms, then a simple integration yields 93% of the signal comes from sodium ions in the lower symmetry site and 7% from the symmetric site. The actual percentage of ions giving rise to the second-order quadrupole broadened signal is somewhat higher because only the central transition is observed. The relative populations did not change over the temperature range investigated.

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The magnetization recovery profiles also yield rapidly equilibrating components that have T_1 values of 500 μs or less. Such short T_1 values are indicative of strong magnetic dipolar relaxation mechanisms between nuclei and unpaired electrons. Paramagnetic dipolar interactions are expected for $Na_{0.7}CoO_2$ since about 30% of the cobalt atoms exist as Co^{4+}. Consequently, all responses are broadened to some degree by dipolar paramagnetic interactions. ^{7}Li NMR studies performed upon Li_xCoO_2[4], have indicated the importance of paramagnetic interactions, which arise from the presence of unpaired electrons localized at Co sites.

Measurements for $Na_{0.3}CoO_2$

Room temperature spectra gathered for $Na_{0.3}CoO_2$ reveal two peaks (Fig. 1): an intense paramagnetically shifted response having a linewidth of about 20 kHz and a weaker diamagnet-ically shifted response with a linewidth less than 10 kHz. Again, integration of the spectrum shows that about 93% of the signal constitutes the intense feature and 7% comes from the smaller feature. The sample has roughly 70% of all the cobalt atoms existing as Co^{4+} (due to the instability of the 4+ oxidation state, this percentage could be less); therefore the spectra are expected to reveal comparatively larger paramagnetic dipolar broadening effects. The intense response does not show resolvable 2nd-order quadrupole divergences (unlike the spectra for $Na_{0.7}CoO_2$) and since the linewidth is smaller than the corresponding line observed for $Na_{0.7}CoO_2$, the sodium sites must be more symmetric and/or the sodium ions exhibit a greater degree of motional averaging.

Lower temperature ^{23}Na NMR responses for x = 0.3 are only slightly broader than the high temperature lines. Nevertheless, linewidths continuously increase down to the lowest temperature measured; the rigid lattice lineshape lies near or below -150° C. T_1 values of the intense component also increase with decreasing temperature and no minima are observed between -150° C to 100° C. T_1 temperature dependence of the small component was not measured. Again, it is clear that motional effects account for the temperature dependence of the response.

T_1s were extracted from two exponential fits, again yielding long and very short values. It is interesting to note that, for a given temperature, T_1 values are larger for $Na_{0.3}CoO_2$ than for

$Na_{0.7}CoO_2$. This implies that the sodium cations in $Na_{0.7}CoO_2$ are more effectively relaxed, than in $Na_{0.3}CoO_2$, due to quadrupolar interactions, which seems plausible given the larger quadrupole broadening observed in the ^{23}Na response. Typically, longer T_1 values range within 20 ms to 200 ms; whereas, the shorter values are around 1 ms - paramagnetic dipolar interactions being responsible for the short T_1s.

Discussion

^{23}Na NMR responses gathered from Na_xCoO_2 samples where x = 0.3 and 0.7 reflect the structural changes of the trigonal prismatic phase as a function of composition. Two features are observed: an intense quadrupolar broadened response, representing about 95% of the sodium ions and characterized by relatively short T_1s; and a weaker narrower response, representing the remainder of the sodium ions, yielding longer T_1s. The weaker response is indicative of sodium ions residing in highly symmetric environments. Given the implausibility of octahedral sites in the structure for x = 0.3 and 0.7, the weaker response is attributed to the presence of an undetermined impurity phase (possibly the octahedral phase or a sodium salt reaction product). This impurity phase was not detected by x-ray diffraction, but its small amount (~5%) being near the detection limit. The quadrupolar broadened response is well resolved for the x = 0.7 indicating that the sodium atoms are somewhat motionally constrained below 100°C. The structural interpretation for the ^{23}Na NMR spectrum with x = 0.3 is less certain because the quadrupolar features cannot be resolved. This line is narrower than expected (in light of strong paramagnetic effects for the sample with more Co^{4+}) indicating greater motion and/or high site symmetry. The argument, suggesting greater cation motion, is in part supported by the temperature dependent lineshapes. Furthermore, an increase in Na^+ mobility for sodium deficient Na_xCoO_2 may be likely, considering an analogous observation made for in Li^- in Li_xCoO_2 [4]. That is, a substantial change in the structure of the P2 phase must take place in order for such changes to occur in sodium site symmetry amd mobility.

Acknowledgements

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Figure Captions

Figure 1. Room temperature spectra (79.63 MHz) for $Na_{0.7}CoO_2$ (top) and $Na_{0.3}CoO_2$ (bottom). (The response near -240 kHz is a [63]Cu artifact from the probe that has been folded into the spectrum.)

Figure 2. Real and simulated lineshapes for 2nd-order quadrupolar broadened response in $Na_{0.7}CoO_2$ at 79.63 MHz (top) and 54.39 MHz (bottom).

Figure 3. $Log(T_1)$ vs. inverse temperature for the intense peak (top) and small peak (bottom).

Figure 4. Spectra illustrating inversion recovery results for $Na_{0.7}CoO_2$. From top to bottom, the recovery times are 3 s, 0.5 s, 10 ms and 5 ms respectively.

Na$_{0.7}$CoO$_2$
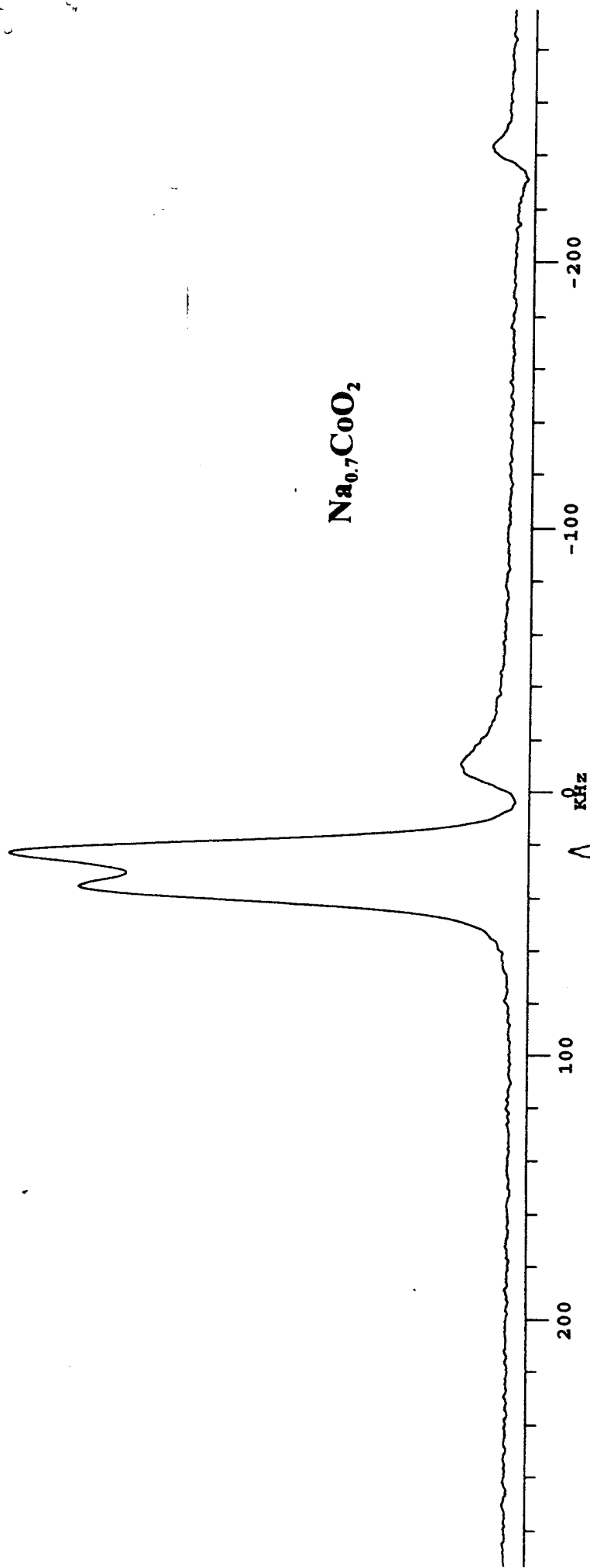
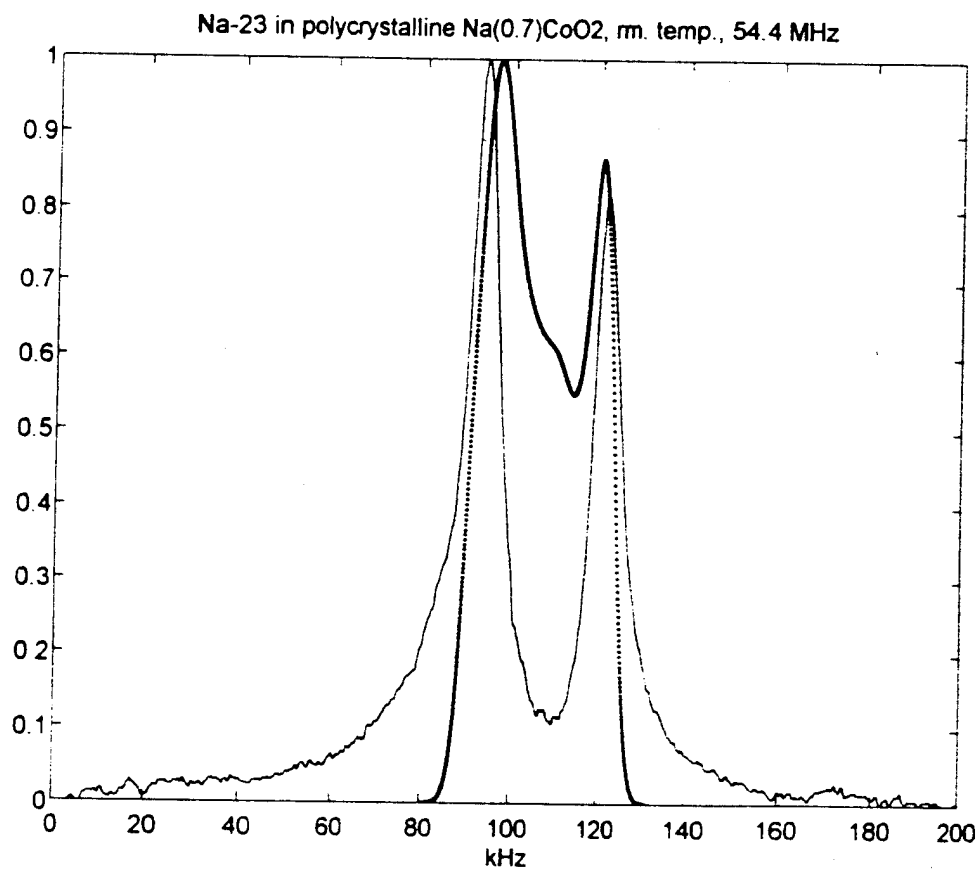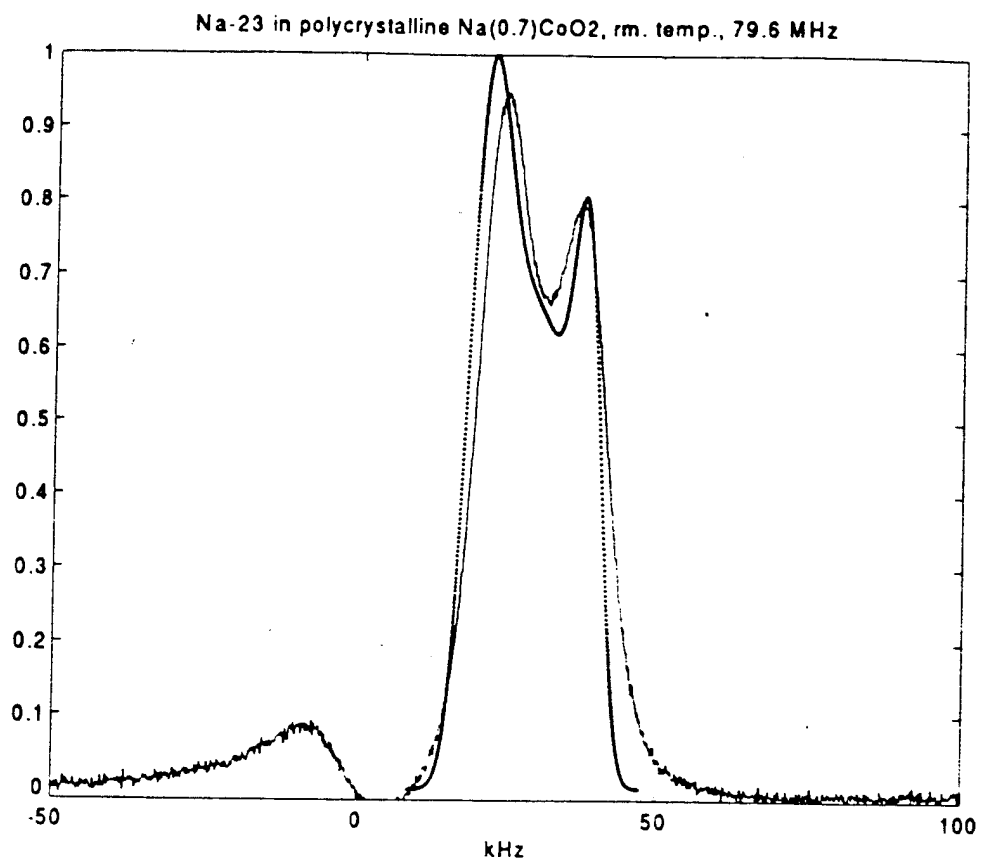Na$_{0.3}$CoO$_2$

kHz

kHz

Na-23 in polycrystalline Na(0.7)CoO2, rm. temp., 79.6 MHz

Na-23 in polycrystalline Na(0.7)CoO2, rm. temp., 54.4 MHz

Fig. 2

Na-23 Log(T1): ● = Na(0.7)CoO2; X = Na(0.3)CoO2
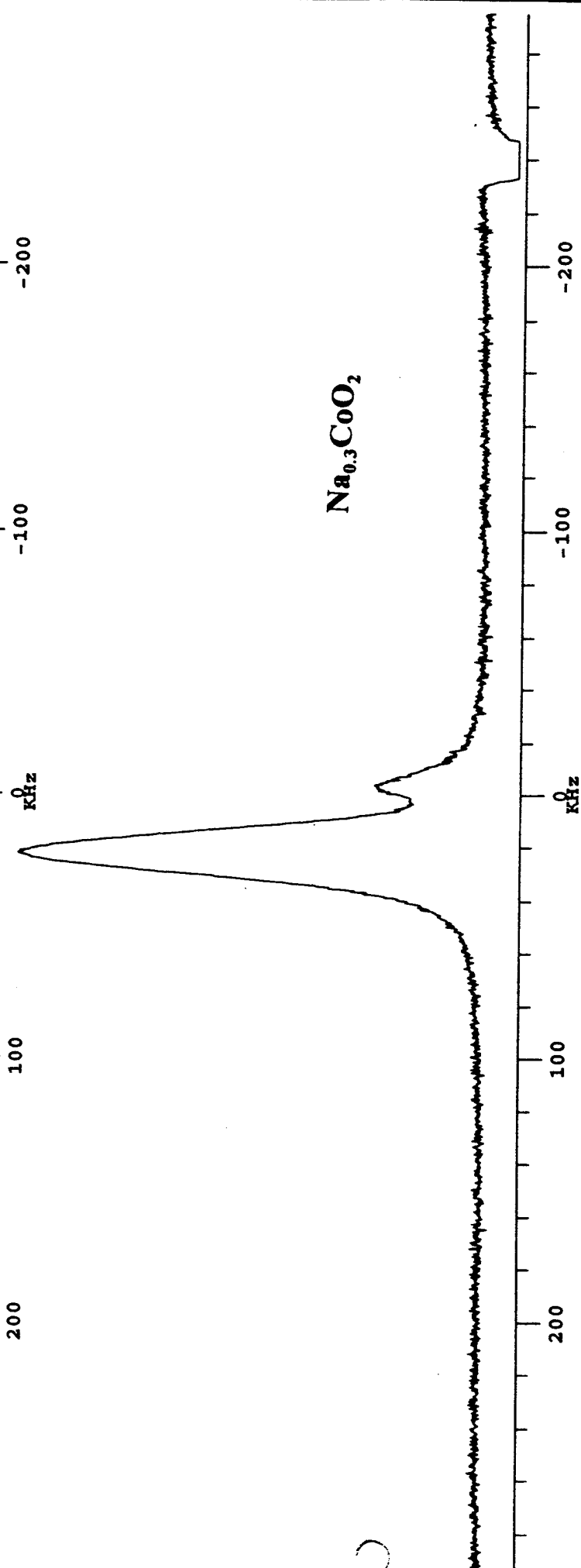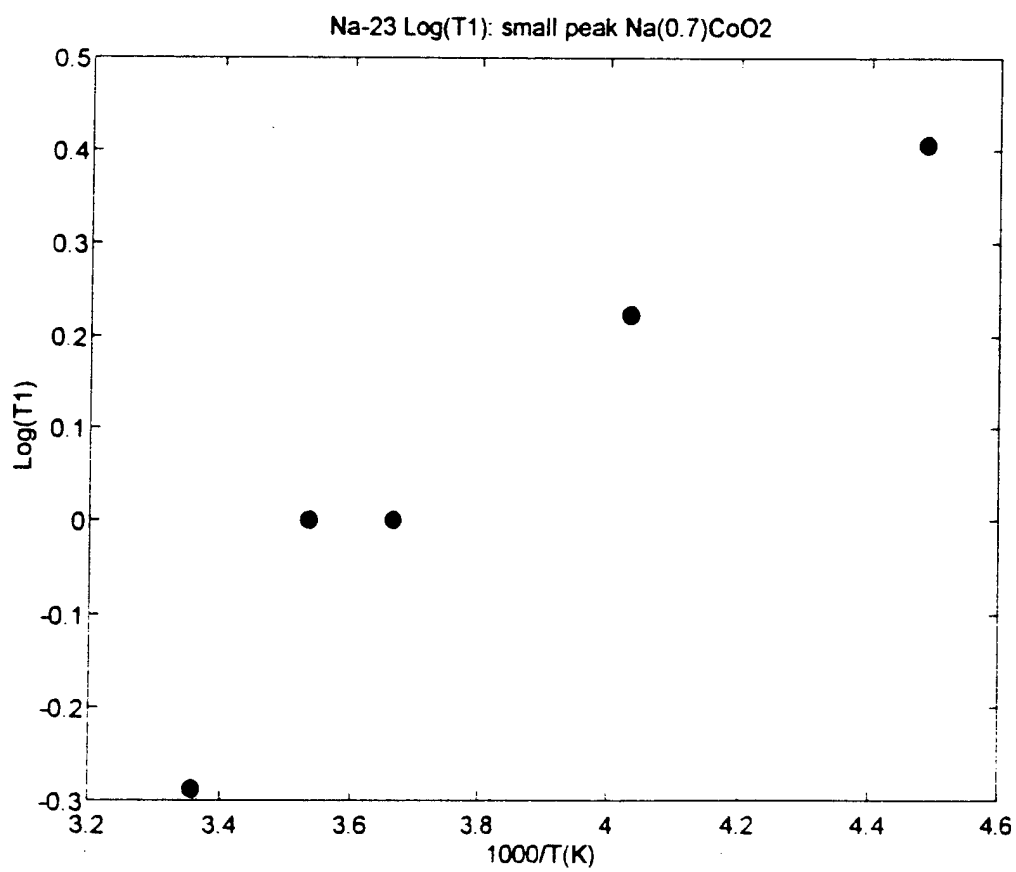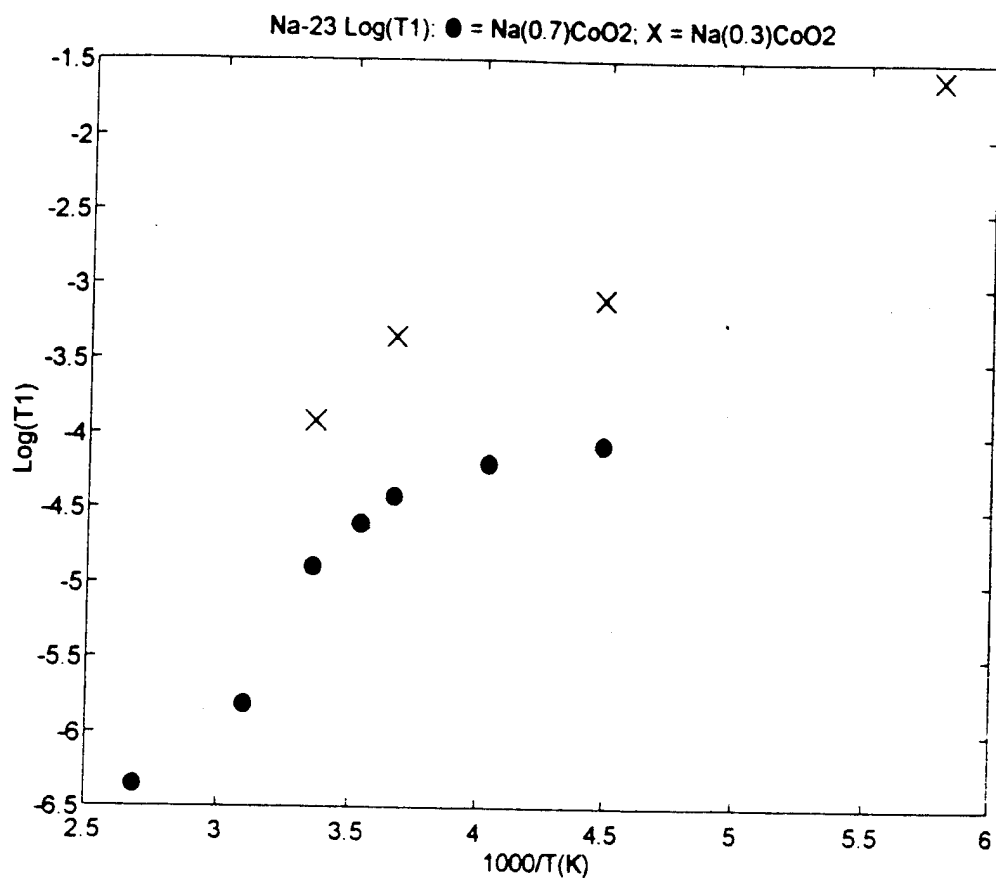
Na-23 Log(T1): small peak Na(0.7)CoO2

Fig. 3

Recovery time = 3 s

0.5 s

10 ms

5 ms

kHz

-200

-100

100

200