# High Temperature *in situ* Raman Spectroscopy of Oxide Species in Molten (Li+K) Carbonate Eutectic

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*In situ* Raman spectra of active oxygen species present in solutions of potassium superoxide ($KO_2$) in (62 + 38) mol% $(Li + K)_2CO_3$ eutectic at 650 °C were observed. We have attempted to obtain vibrational spectra of these entities by surface enhanced Raman scattering (SERS) technique.

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The further development of the molten carbonate fuel cell (MCFC) requires a through knowledge of the oxide chemistry in the melt. In particular, experimental verification of active oxygen species responsible for the oxygen reduction has been a long-term issue. The oxygen reduction in molten carbonate is a key reaction for the development of MCFC. As yet, only the quenched samples of carbonates were investigated with spectroscopic techniques.[1,2] Electron spin resonance (ESR) appeared to be sensitive enough to identify the response from $O_2^-$ ions even in the samples without extra addition of superoxide to the melt.[2] However, this technique is useless for detecting peroxides whose resultant electron spin equal to zero. Therefore, Raman spectroscopy, which is less sensitive but applicable to high temperature melts, can be employed for this purpose. Furthermore, the phenomenon of SERS provides information about the surface species on the electrode material, e.g. silver and gold and is practicable for verifying the presence of species at low concentrations. In this work, we present Raman spectra obtained with a new experimental method (SERS) applied to molten carbonates for the first time.

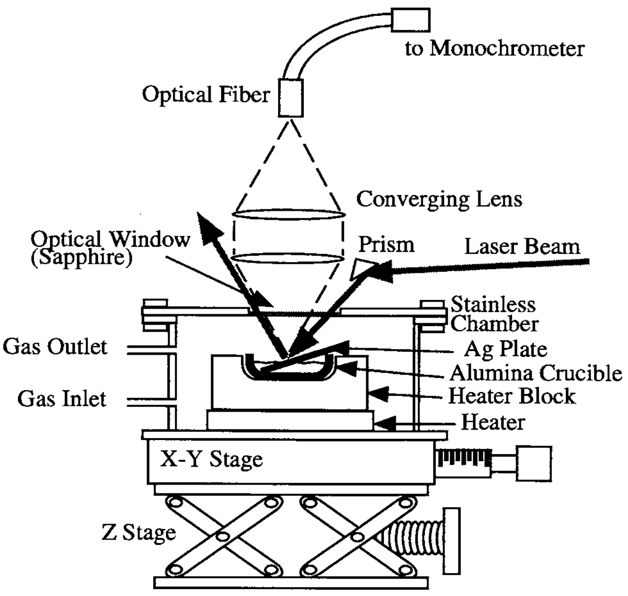

**Figure 1.** Schematic illustration of the cell structure of in situ Raman spectroscopy for molten carbonates.

The cell used for *in situ* Raman spectroscopy at high temperatures is shown in Figure 1. The exited laser beam (514.5 nm, 300 mW) of an argon ion laser (Coherent, Innova 70) entered the cell throughout a sapphire crystal window of 300 μm thickness. The same window allowed leaving the light scattered on silver surface, which afterwards was collected by lens and focused on the edge of an optical fiber. Finally, this scattered light was dispersed by means of a triple stage monochrometer (Jasco TRS-300). The effective spectral width was ca. 32 $cm^{-1}$ and ca. 150 s was needed to accumulate the Raman data. Black body radiation due to high temperatures and dark currents of the detector were determined and subtracted from the apparent spectra.

The preparation procedure of (62 + 38) mol% $(Li + K)_2CO_3$ melt has been described previously.[3,4] The melt container was made of pure alumina (SSA-S grade, Nippon Kagaku Togyo). A silver disk (5x10 $mm^2$, 1.0 mm thickness) was 99.99% polycrystalline sample. To obtain a specular surface, the sample was polished with 0.1 μm alumina powder and subsequently etched slightly in 10% $HNO_3$ aqueous solution. The experiments were performed at 650 °C under an atmosphere of gas mixture $O_2/CO_2$ = 9/1. When potassium super oxide ($KO_2$, Aldrich) was added into the melt, special care was paid to avoid contacting with moisture in the air.

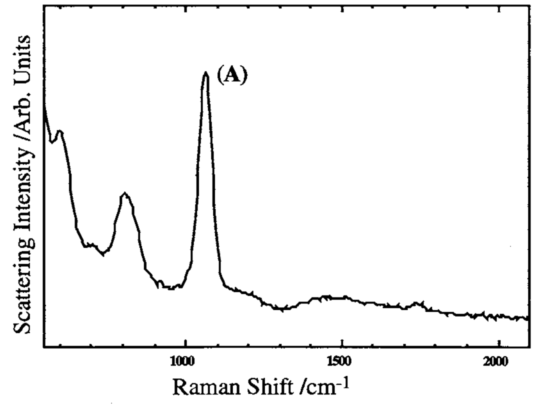

**Figure 2.** Raman spectrum of (62+38) mol%$(Li + K)_2CO_3$ carbonate eutectic at 650 °C. Gas atmosphere is $O_2/CO_2$ = 9/1.

The Raman spectra of the pure (Li + K) carbonate eutectic is shown in Figure 2. The vibrational frequency of 1065 $cm^{-1}$ of the predominated Raman line (A) is similar to those for $CO_3^{2-}$ ions in solid phase and hydrated ions in aqueous solutions.[5] In consequence, this Raman line can be attributed to the symmetric stretching vibration of $CO_3^{2-}$ ions in the carbonate melt. Unfortunately, we are not able to distinguish between the responses of carbonate ions and oxygen species dissolved in

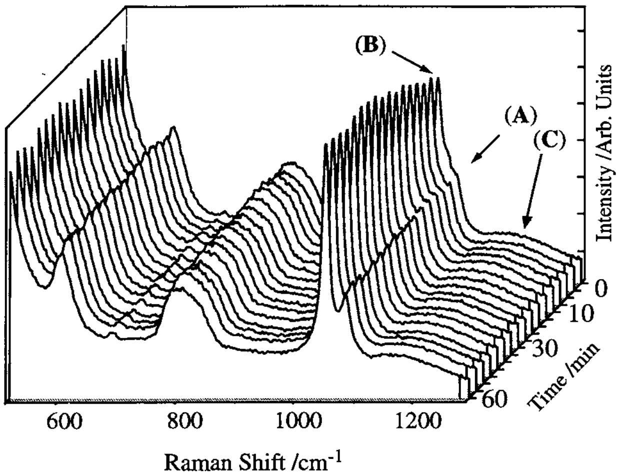

**Figure 3.** Variation of Raman spectra with time after adding $KO_2$ into the carbonate melt at 650 °C. Gas atmosphere is $O_2/CO_2 = 9/1$.

molten carbonates.

Figure 3 presents variation of Raman spectra with time after adding $KO_2$ of approximately to 0.1 mol% into the carbonate melt. Apart from already observed line assigned to $CO_3^{2-}$ vibration, new lines appear at (B) 1047 cm$^{-1}$ and (C) 1185 cm$^{-1}$.

By the use of SERS effect in UHV (Ultra High Vacuum), Pettenkofer *et al.* reported the Raman lines due to the oxygen molecules adsorbed on a silver film.[6] In this report, one of the lines observed at 1053 cm$^{-1}$ was assigned to the stretching vibration of the oxygen species in the form of superoxide ions. This is most straightforward evidence for the line observed at 1047 cm$^{-1}$ in this work.

Wang *et al.*[7-9] have analyzed the RAIRS (Reflection-Absorption Infrared Spectroscopy) data obtained for various oxygen species adsorbed on a silver surface in UHV. They have discussed the relation between the vibrational frequency and the number of electrons in π* orbital. In conclusion they have evaluated the dependence of the O-O force constant on $q$ in $O_2^{q-}$ or alternatively on the π* occupancy. Taking into account that the frequency of O-O stretching vibration is proportional to the number of electrons in π* orbital, we could identify the observed Raman line at 1047 cm$^{-1}$ with that due to the O-O molecular vibration of the superoxide.

*In situ* Raman investigations of the interface between the silver and molten (Li + K) carbonate eutectic were performed at 650 °C. New lines observed after adding $KO_2$ to the melt were analyzed and discussed. The line of frequencies 1047 cm$^{-1}$ was identified with the vibration of superoxide ions in the melt. Further work is required to obtain more detailed pictures of the oxide chemistry in molten carbonates by using this Raman spectroscopic technique.

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## References and Notes

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