

Interfacial conductivity observation of CaF₂ ionic conductor films using Lewis-acidic effect

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CaF₂ polycrystalline films were treated with a Lewis acid to form a space charge layer of F⁻-vacancies at the adsorbed interface. After the adsorption of SbF₅ molecules on the film, the impedance spectra changed from one semicircle to two semicircles. Investigation of these impedance results, combined with the equivalent circuit models, suggest that the high-frequency semicircle may be ascribed to the high conduction layer connected in parallel with bulk conduction and the low frequency semicircle suggests the blocking effect of a perpendicular barrier for the current flow. Numerical estimation is reasonably consistent with this model. This confirms that space charge layers composed of ion vacancies can be systematically created using the chemical attractive force of Lewis acids.

1. Introduction

Ionic conductors are modern materials applicable to solid electrolytes in solid state batteries, electrochromic devices and gas sensors because of their stability and simplicity for treatment and fabrication compared with conventional liquid electrolytes [1–3].

The preparation of composite conductors by heterogeneous doping is an effective method of enhancing conductivity. Several ionic conductors, such as alkali halides and a sodium zirconium silicate, Na₄Zr₂Si₃O₁₂, showed a conductivity increase of more than one order of magnitude due to the dispersion of insulator particles of a second phase such as alumina or silica [4–8]. The mechanisms responsible for this enhancement were classified into two categories, that is, the interfacial mechanisms and matrix mechanisms, where the latter means that a micro- and/or macrostructural change in the bulk affect the original bulk conduction. In the case of interfacial conduction, it is widely accepted that a new type of conduction layer contributes to the conductivity enhancement, that is, space charge regions which consist of an enhanced number of defects, vacancies and interstitials.

In the present study, based on the concept of an interfacial conduction model, a gas adsorbate, SbF₅, was used as a second phase because it has a predictable chemical effect [7, 10]. As an ionic conductor, CaF₂ films were used. CaF₂ shows Frenkel disorder in the fluoride sublattice and exhibits significant anionic conduction [11]. The lower temperature region below ~850 K was identified as an extrinsic region due to vacancies induced by impurities such as oxygen [12]. Therefore, if the SbF₅ Lewis acid, which has the characteristic of F⁻-anion attraction, adsorbs on CaF₂, the conductivity could be enhanced due to the increase in fluoride-ion vacancies along the adsorbed interface. Furthermore, enhanced

conductivity has been quantitatively estimated based on an equivalent circuit model. The CaF₂ film covered with SbF₅ adsorbates supplies a simple (two dimensional) morphological interface, and is suitable for the quantitative estimation of the interfacial conductivity.

2. Experimental details

CaF₂ polycrystalline films with thicknesses of 600, 900, 600 and 700 nm were prepared by vacuum evaporation of high purity grade CaF₂ (99.95%, Johnson Matthey) onto high purity quartz substrates carrying interdigital gold electrodes with 20 μm spacing, which give a cell constant in the range of 0.379 cm⁻¹ to 0.175 cm⁻¹. The surface condition and porosity of the films were checked using scanning electron microscopy (SEM). The SbF₅ Lewis acid was adsorbed on the film by exposing the vapour at about 0.1–0.5 bar and 673 K. The adsorption system has been previously described [13]. The adsorption and evacuation processes were repeated several times to confirm the chemical adsorption.

The impedance spectra were measured using HP4192 and HP4284 frequency analysers in the frequency range 5 Hz to 1 MHz.

3. Results and discussion

XRD patterns of the CaF₂ were consistent with that of polycrystalline ceramic CaF₂, indicating that the film is polycrystalline without any detectable uniaxial crystal growth. The films thicker than 600 nm with acid treatment showed no additional XRD peak except CaF₂, indicating that no chemical reaction between CaF₂ and SbF₅ occurred. In the case of CaF₂ films of 300 nm thickness, some additional reflections appeared after several heating cycles. This is probably due to the chemical reaction with SbF₅

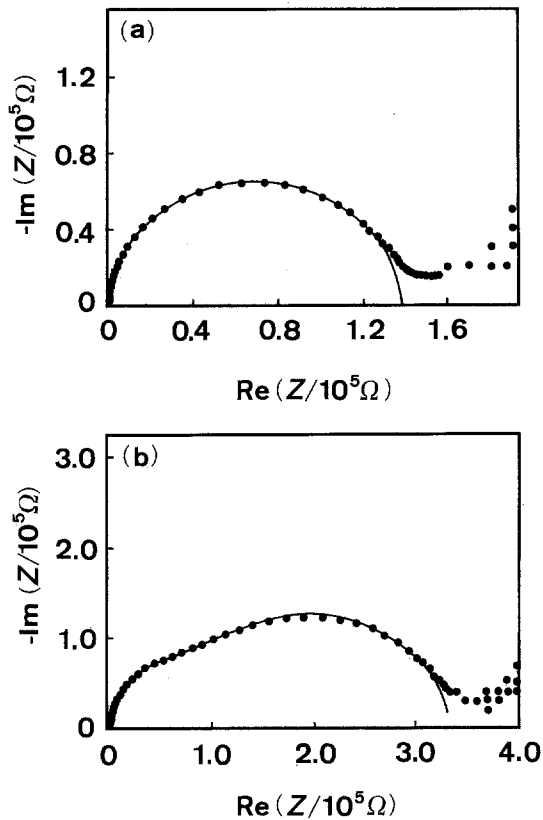


Fig. 1. Typical impedance spectra of a pure CaF_2 film (a) and a SbF_5 -treated CaF_2 film (quartz substrate, 600 nm thickness) in the frequency range of 5 Hz–1 MHz at 300°C. The capacitances estimated from the top of the semicircle are: (a) 20 pF, and (b) 20 pF and 300 pF for high frequency and low frequency semicircles, respectively.

penetrating into the micropores at the thin film surface. For this reason, films thicker than 600 nm are mainly discussed in this study.

The impedance spectra of the pure CaF_2 films consist only of one semicircle (Fig. 1(a)). The effective dielectric constant is ~ 20 pF, almost three to five times higher than that for polycrystalline ceramics. This is due to the addition of the capacitance attributable to the quartz substrate and to an increase in the grain boundary contribution to the total electrical property associated with the film morphology [14].

The conductivity is independent of film thickness in the range 300 to 900 nm, and is reproducible. The conductivity variation above 650 K is slightly steeper compared with the polycrystalline ceramic CaF_2 with an activation energy of 1.1 eV [13, 15]. These impedance results also suggest that the films have almost the same polycrystalline morphology as the ceramic conductor CaF_2 , which is consistent with the XRD results.

After the adsorption of SbF_5 on the 600 nm and 900 nm thick CaF_2 films, the impedance spectra showed two semicircles (Fig. 1(b)). The capacitances were 30 pF and 200 pF for the high frequency and low frequency semicircles, respectively.

This impedance behaviour follows the behaviour described for previously analysed polycrystalline or composite systems [3]. The high frequency semicircle is characterized by the combination of bulk

conductivity and the contribution from the high conduction layers in parallel. This case, in which no compound formation was observed and the absolute resistance value from the high frequency semicircle decreased, obviously suggests that gas adsorbates have created the high conduction layer. The low frequency semicircle, on the other hand, is determined by the blocking of the aforementioned pathways in series [3]. This contribution is ascribed to the grain boundary core structure and the gas molecules adsorbed therein, or a partial insulating thin compound being perpendicular to the current flow.

Therefore, this situation may be simply represented by the equivalent circuit shown in Fig. 2(a). Due to the low capacitance value of the high conduction layer, the bulk capacitance predominantly determines the peak frequency of the high frequency semicircle. Figure 3 shows a schematic representation of the film with typical conduction contributions. The real conductivity of each part can be represented as

$$\sigma_{\infty} = (1/R_{\infty}) \times (d/S) \quad (1a)$$

$$\sigma_{\parallel} = (1/R_{\parallel}) \times (d/S') \quad (1b)$$

$$\sigma_{\perp} = (1/R_{\perp}) \times (d'/S) \quad (1c)$$

where, σ_{∞} , R_{∞} ; σ_{\parallel} , R_{\parallel} ; σ_{\perp} , R_{\perp} are conductivities and resistances of the bulk, the high conduction layer, and blocking layer, respectively. S and d are the area and distance of the interdigital electrode, respectively. Real geometrical factors of area S' for the high conduction layer and distance d' for the blocking

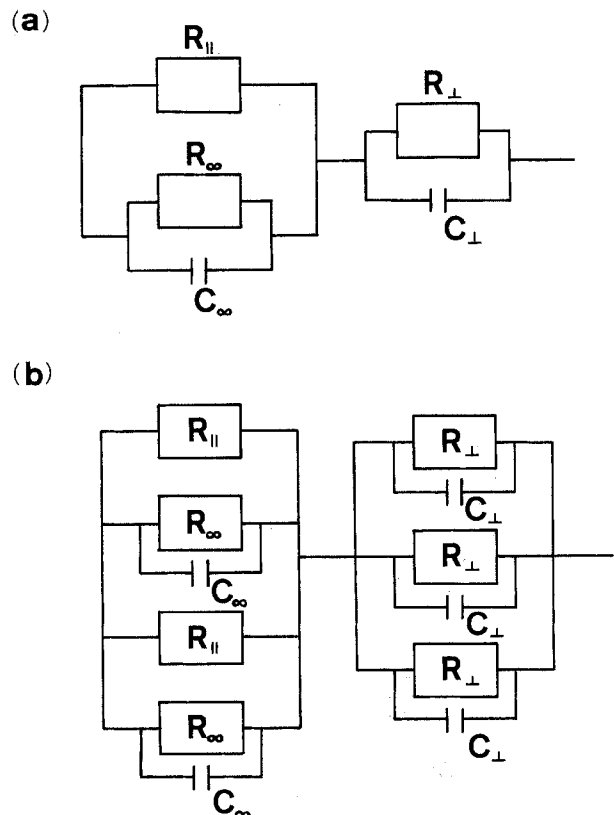


Fig. 2. Predictable equivalent circuit of (a) CaF_2 film treated with SbF_5 and (b) sandwiched film treated with SbF_5 (SbF_5 - CaF_2 - SbF_5 - CaF_2 layer contains double contributions of the bulk (R_{∞}) and high conduction layer (R_{\parallel}), and triple blocking effect (R_{\perp}).

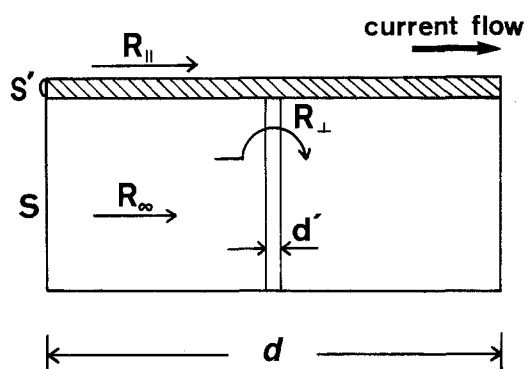
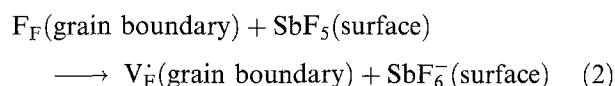


Fig. 3. Schematic feature of the film with contributing resistances and geometrical factors: R_{∞} = bulk resistance; $R_{||}$ = high conduction layer resistance; R_{\perp} = the resistance of blocking due to grain boundary and adsorbates; d = distance between electrodes; S = surface area of electrode; d' = the width of real blocking layer; S' = effective area of high conduction layer.

effect will be smaller, as indicated in Fig. 3. However, it is impossible to quantitatively estimate these parameters because they depend on the film condition, which is influenced by the preparation process. Therefore, the temperature dependencies of the conductance corresponding to each semicircle are plotted in Fig. 4. The activation energies from each contribution are almost the same as that of pure CaF₂. The conductance estimated from the high frequency semicircle was also higher than that of CaF₂ without SbF₅ adsorption. These results suggest that space charges enriched with fluoride-ion vacancies are responsible for the high conductive layer estimated from the high frequency semicircle. The vacancy formation mechanism at the interface between CaF₂ and SbF₅ may be described as



where F_F is the fluoride ion at the fluoride site and V_F^- is the fluoride ion vacancy at the fluoride site. The effect of nominal homogeneous doping (e.g., Sb⁵⁺-ion substitution for Ca²⁺-ion) can be excluded because this would result in an interstitial F⁻-ion increase and drastically change the activation energy for ion conduction by the dominant interstitial mechanism [1]. Estimation of the conductivity enhancement assuming a single interface due to vacancy enriched space charges has already been discussed [13].

The conductance change obtained from the low frequency semicircle shows a slight hysteresis during the heating cycle (Fig. 4). This may be due to a partial desorption of adsorbed acid species after heating the sample to 773 K. The similarity in the activation energy of both processes to the bulk value, however, suggests a current narrowing effect by nonideal contacts as found and analysed in ceramics [16].

In the cooling process during impedance observation, the division of the two semicircles became unclear, indicating that the relaxation time of the two processes approach each other [13]. When this

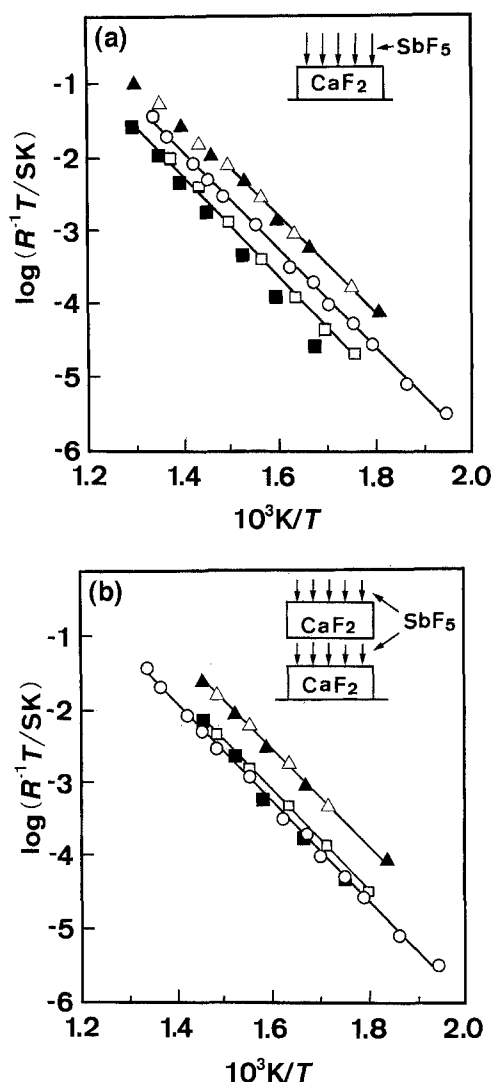


Fig. 4. (a) Temperature dependence of conductances of untreated CaF₂ film (circle) and the SbF₅-treated film for the heating (filled) and cooling (unfilled) temperature processes. The conductance obtained from the high frequency semicircle (triangle) shows the vacancy conduction activation energy in the temperature region between 250 and 400 °C. The conductance obtained from the low frequency semicircle (square) shows a hysteresis in the heating cycle process. (b) Temperature dependence of conductances of untreated CaF₂ film (circle) and the SbF₅-treated sandwiched film from high frequency semicircle (triangle) and from the low frequency semicircle (square) composed of heating (filled) and cooling (unfilled) temperature processes.

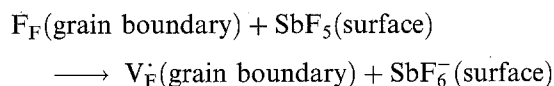
SbF₅-treated film is covered with a CaF₂ film, resulting in the formation of a 'sandwiched film' providing desorption barriers, the impedance and the capacitance values from the high and low frequency semicircles did not change even after several heating cycles [13]. Therefore, it is clear that the relaxation time change of the 'single film' derives from desorption rather than from grain growth by heating.

The resistance values corresponding to three components of the equivalent circuit were estimated (Fig. 2(a)) by fitting to the conductance observed in Fig. 4(a). At 625 K, $R_{\infty} = 1.4 \times 10^6 \Omega$, $R_{||} = 7.8 \times 10^5 \Omega$, and $R_{\perp} = 3.6 \times 10^6 \Omega$ for the bulk, high conduction and blocking resistances, respectively, where R_{∞} is independently estimated from the data of the untreated pure CaF₂ film.

After the SbF_5 treatment of the sandwiched film ($\text{SbF}_5\text{-CaF}_2\text{-SbF}_5\text{-CaF}_2$), the equivalent circuit of this situation may be represented in Fig. 2(b). This configuration presumes the resistances estimated from the two semicircles, using R_∞ , R_\parallel and R_\perp obtained above, to be $R_h = 2.5 \times 10^5 \Omega$ and $R_1 = 1.7 \times 10^6 \Omega$ for the high frequency and low frequency semicircles at 625 K, respectively. On the other hand, the observed conductance values in Fig. 4(b) give the same resistance, $R_h = 2.5 \times 10^5 \Omega$, and a different value, $R_1 = 9.6 \times 10^5$, at the same temperature. The obtained R_h value is consistent with the equivalent circuit model. The difference between the observed and the expected R_1 values is mainly due to the adsorbates between the two films. Overlapping the second layer would affect the insulating block to release the barrier for ionic migration because of the micro morphological change. However, these results are reasonably consistent with the model of the original equivalent circuit composed of the bulk, high conduction layer and blocking effect. It can be concluded that the SbF_5 adsorbates induce the F^- -ion vacancies which are responsible for the enhanced conductivity appearing in the high frequency semicircle. The adsorbates also lead to blocking for ionic conduction, which is confirmed by the low frequency semicircle.

4. Conclusions

Adsorption of SbF_5 Lewis acid on the CaF_2 film produced a change in the impedance spectra which contain two semicircles. Analyses of the observed impedance data associated with the equivalent circuit model confirmed that the impedance change is due to the formation of a high conduction layer at the adsorbed interface which is connected to the bulk contribution in parallel. The formation mechanism of the high conduction layer may be expressed as



That is, adsorbed Lewis acids, SbF_5 , attract fluoride ions out of the CaF_2 boundary regions to create fluoride ion vacancies (V_F^-) at the $\text{CaF}_2/\text{SbF}_5$ interfaces. It is expected that the counter-charge results in SbF_6^- anions at the surface. It also appeared that the low frequency semicircle came from the blocking effects due to the grain boundary core structure and adsorbates after SbF_5 adsorption.

This result is an initial success to encourage the space charges of mobile ion defects using the chemical attractive force of acids for conductivity enhancement.

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