

Prediction and verification of Li^+ charge transfer at LiF/TiO_2 interfaces

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In nanoscale systems, contributions of interfaces can easily determine the overall properties. This led to the development of heterogeneous electrolytes. A rather universal mechanism relies on the generalized space charge picture developed in Stuttgart that accounts for both redistribution of ionic and electronic charge carriers in equilibrium.

The present example to study ionic and electronic conductivity properties of LiF films on TiO_2 substrates is remarkable in two aspects: (i) The variation of film thickness allows for a clear separation of bulk and interface contributions and (ii) more importantly: this system is the first system in which the direction of the ionic charge carrier redistribution was predicted and then fully verified [1]. There is a third reason of studying LiF: In spite of their practical importance (batteries, fuel cells) and recent encouraging results, the field of heterogeneous electrolytes conductive for the light cations Li^+ and H^+ is not adequately explored. In view of its stability, low carrier concentration, but significant mobilities of both cation and anion, we decided to study LiF as a platform material [2]. Fortunately, its defect chemistry is rather simple and primarily characterized by Schottky disorder with a significant ionic gap corresponding to intrinsically low carrier densities of lithium and fluoride vacancies (V'_{Li} and V^{\cdot}_{F}). The LiF films were prepared by radio frequency sputtering without *in-situ* heating from a single-crystal LiF target. In view of low intrinsic disorder, the electrical behavior is expected to be sensitively influenced by the surface chemistry of respective oxide substrates [3], contributing enormous richness of interfacial defect chemistry in terms of generalized space charge models as well as its relevance for the overall material properties.

In essence, as far as LiF is concerned, Li^+ deficiency (not Li deficiency!) is easily feasible rather than Li^+ excess. On the other side, we know that titania is able to accommodate small cations such as Li^+ or H^+ species. This ability to take up Li^+ is obvious from its functioning as a powerful anode (Li storage is sufficient but not necessary for Li^+ accommodation. Note that in our example, in the absence of any redox process, we are not concerned with $\text{Li} = \text{Li}^+ + e^-$ incorporation, rather we deal with a pure ionic effect.) As both lithium vacancies in LiF and lithium interstitials in TiO_2 possess rather low energies, the contact LiF/TiO_2 is expected to lead to a Li^+ transfer from LiF to TiO_2 . First of all this should give rise to increased lithium vacancy conductivity in LiF [1]. Correspondingly the compensating excess charge in TiO_2 is represented by lithium interstitials. This excess charge results in a field that leads to depletion of excess electrons and accumulation of holes in TiO_2 . Owing to the comparatively high electronic conductivities in TiO_2 the electronic will prevail over the ionic effect there in complete contrast to LiF. As will be shown we indeed observe increased Li-vacancy conductivity in LiF as well as switch-over from n- to p-type conductivity on the TiO_2 side. This not only fully supports the space charge model but also shows the predictive power of the model of heterogeneous doping.

The LiF thin films are highly textured with [100] as preferred direction on titania (100) substrate from the X-ray diffraction (XRD) pattern. Cross-sectional transmission electron microscopy (TEM) image discloses an island-type rather than sheet-type growth mode from the columnar LiF thin films. The voids or grain boundaries between the adjacent epitaxial columnar crystallites are caused by the different in-plane azimuthal rotation of the crystallites. Figure 1 displays the expected space charge effect of the LiF- TiO_2 interface. As already briefly touched upon, a transfer of Li^+ from LiF to TiO_2 should lead to an accumulation of Li interstitials (Li') on the substrate side, while lithium vacancies (V'_{Li}) should be accumulated on the LiF side. The distribution naturally restricts to the respective space charge zones. As a consequence of the space charge field, conduction electrons (e') are expected to be depleted at the TiO_2 side, while the concentration of holes (h') should be increased. Although in minority, the electronic defects are expected to dominate the overall conductivity in TiO_2 . Therefore, we use two different electrode configurations. The ionically blocking one is made of sputtered Pt. Pt dendrites that fully penetrate the LiF film serve as microelectrodes with the help of which we are able to detect electronic contributions of the titania subsurface. In order to measure Li^+

conductivity on the same samples we polished off the Pt coating, then applied electronically blocking electrodes each consisting of a thin layer of the ionically conductive ceramic $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LATSP) and a thin layer of the redox couple $\text{LiFePO}_4\text{-FePO}_4$ (to which carbon is admixed) atop. Simultaneously, this configuration will also block out F^- contributions.

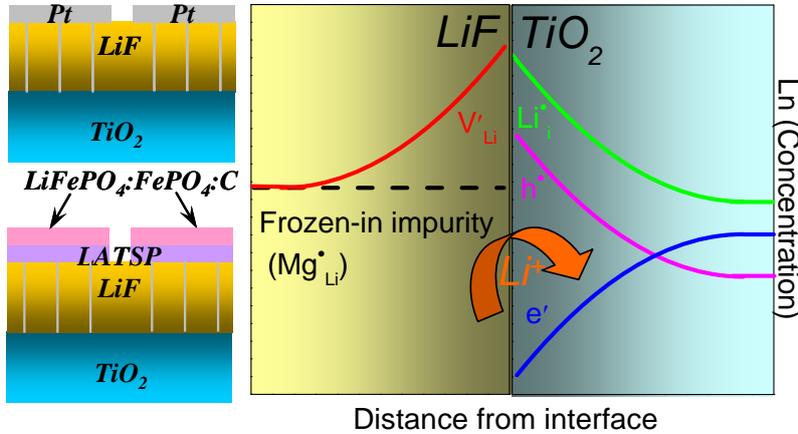


Figure 1. (Left) Both ion- and electron-blocking measurement architectures of LiF-TiO₂ prototype. (Right) Overview defect chemistry schemes and carrier concentration profiles of LiF/TiO₂ interface. Reprinted with permission from Ref [1]. Copyright 2012. American Chemical Society.

The ion-conductive effect of the interface is seen when $Y_{ion}^{||}$ ($Y_{ion}^{||}$ being normalized parallel conductance) is plotted as a function of L (L being film thickness) in Fig. 2(a). The normalized conductance decreases linearly with decreasing layer thickness, but with a positive extrapolated intercept with the y axis. Based on $Y_{ion}^{||}(L) = \sigma_{ion\infty}L + \Delta Y_{ion}^{||}$, with $\sigma_{ion\infty}$ and $\Delta Y_{ion}^{||}$ being bulk conductivity and excess conductance value (positive or negative for accumulation or depletion effect) respectively, we can deduce $\Delta Y_{ion}^{||}$ and $\sigma_{ion\infty}$ from the linear relation of $Y_{ion}^{||}(L)$. The bulk conductivity $\sigma_{ion\infty}$ of LiF thin films at 190°C is estimated from the slope to be about 2.8×10^{-7} S/cm, which is consistent with the literature values of lightly doped single-crystal ($10^{-7} \sim 10^{-6}$ S/cm) at this temperature. $\Delta Y_{ion}^{||}$ obtained from the intercept by extrapolating the linear fitting of $Y_{ion}^{||}(L)$ to $L = 0$ is positive, indicating ion carrier accumulation. Both the Arrhenius plots of $\sigma_{ion\infty}$ and $\Delta Y_{ion}^{||}$ deduced from different ambient temperatures are shown in Fig. 2(b), respectively. In accordance with the interfacially induced Li^+ -accumulation, $\sigma_{ion\infty}$ is a little lower than the overall conductivity at the corresponding temperatures. The similar activation energies (~ 0.65 eV) for $\sigma_{ion\infty}$ and $\Delta Y_{ion}^{||}$ indicate invariant Li^+ mobility in both the bulk and interface regions.

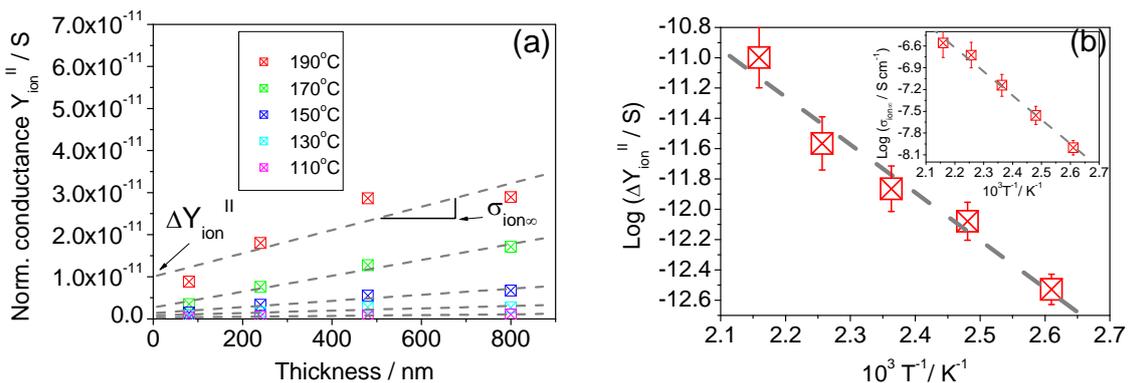


Figure 2: (a) Normalized ion conductance plots as a function of thickness measured at various temperatures (110~190 °C), $\sigma_{ion\infty}$ and $\Delta Y_{ion}^{||}$ denote bulk conductivity of LiF and excess conductance of charge-accumulated effect. (b) Arrhenius plots of excess conductance value ($\Delta Y_{ion}^{||}$) deduced from (a), inset of (b): Arrhenius plots of bulk conductivity ($\sigma_{ion\infty}$) also deduced from (a). LiF thin film samples use LATSP and $\text{LiFePO}_4\text{-FePO}_4\text{-C}$ as electron blocking layer and Li-insertable electrode respectively (electron-blocking structure). Reprinted with permission from Ref [1]. Copyright 2012. American Chemical Society.

Let us turn to the Pt-electrodes, which leak through LiF. These Pt-dendrites probe sensitively the titania surface with a detection radius of 10~20 nm (dendrite diameter). Even though there might be a variation of the defect density by a small amount of lithiation, the increased electron conductivity in titania is primarily due to the expected space charge effect as a consequence of Li^+ transfer. This is

unambiguously shown by studying the P_{O_2} -dependence (Fig. 3) which clearly indicates p-type conductivity. For pure substrate, the slopes from logarithmic plots of conductance as a function of $\log(P_{O_2})$ are around $-1/4$, agreeing with that of n-type conduction in Schottky disordered TiO_2 in mild reduction regime. When TiO_2 is covered by LiF, however a positive slope is observed, especially close to $1/4$ at higher temperature and thinner coverage, indicating a conversion to p-type conduction. (It is important to state that even though the exponents will generally not be the same as in the bulk, we expect $+1/4$ also in the space charge zones if the electronic carriers are in the minority with respect to ionic defects.) The conductivity-increase on P_{O_2} increase is significant if the kinetics enable at least partial equilibration. The flat behaviour at low temperature in Fig. 3(b) is not due to proximity to the n-p transition rather due to sluggish kinetics as the hysteresis shows. While Li transfer would result in increased n-type conductivity, the increased p-type conductivity observed clearly shows the dominance of the Li^+ transfer under concern. The fact that P_{O_2} effects are better defined for very thin films is certainly due to a better oxygen diffusion through the thin LiF films. The observation that the conductance is higher and also the response to P_{O_2} changes quicker for thinner films can be ascribed to a higher fraction of percolating dendrites and pinholes.

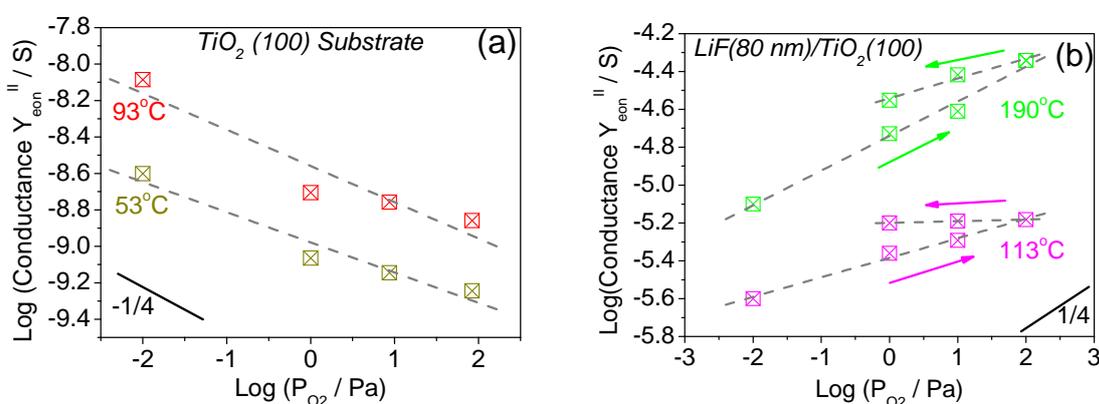


Figure 3: Logarithm plots of conductance as a function of P_{O_2} logarithm at various testing temperatures for (a) pure TiO_2 substrate and (b) $LiF(80 \text{ nm})/TiO_2$ sample, derived from the semicircle intercept of corresponding AC impedance curves of ion-blocking construction. Reprinted with permission from Ref [1]. Copyright 2012. American Chemical Society.

In summary, highly textured LiF thin films have been grown on titania (100) surface, and electrically investigated in both ion- and electron-blocking measurement architectures. Film thickness variation is exploited as a major tool to separate bulk and boundary effects. It is noteworthy that both the ionic accumulation effect in LiF and the accompanying effect on the electronic space charge distribution in TiO_2 have been predicted and verified. Hence, this LiF/ TiO_2 example fully confirms the heterogeneous doping model. It moreover is a decisive step forward in deliberately selecting solid/solid contacts in order to achieve a desired ionic/electronic effect. Such ionic and electronic redistribution effects depending on ionically determined space charge potentials are highly relevant not only for issues of ion and electron transport but equally for chemical reactivities, in particular catalysis.

References:

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