Linking the Chemistry and Physics of Electronic Charge Transfer in Insulators: Theory and Experiment

Richard P. N. Veregin,[a] Michael S. Hawkins,[a] Qingbin Li,[b] Sergey Gusarov,[b] and Andriy Kovalenko,[b,c]; [a]Xerox Research Centre of Canada, Mississauga, Ontario, Canada; [b]National Institute for Nanotechnology, Edmonton, Alberta, Canada; [c]Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada

Abstract

The surface states model is successful in predicting many salient features of charge transfer in insulative materials, which is critical to electrophotography. This paper will discuss how the surface chemistry controls the physics, the chemical potentials, and how it fits the surface states model. The interrelationship of acid-base K_a/K_b values of the materials in contact, measured by IGC (inverse gas chromatography), the HOMO (highest occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) and their excited states calculated using DFT (density functional theory) quantum mechanical modeling, the chemical potentials measured by the Kelvin method, and triboelectric charging data are studied. It will be shown that a precursor complex of the contacting materials, prior to the charge transfer event, can be calculated by DFT to predict both qualitatively and quantitatively triboelectric charging. The work focuses on PTFE, Kynar and PMMA polymers, as well as silica, titania and alumina.

Introduction

The surface states model[1] has been successful in explaining the physics behind charge exchange in insulators, predicting accurately many of the salient features of charging. The weakness of the model is that it is silent on the nature of the surface states responsible for charge exchange, and even the nature of the charge species itself—ions or electrons. The bidirectional Lewis acid-base charge model[2,3] was introduced to address this issue, to provide a chemical basis for the electron donors and acceptors in an electronic charge exchange mechanism for insulators. While this model fits within the surface states model, it suggests discrete donor and acceptor states, not the continuous inter-gap states postulated by the surface states model. More recently molecular modeling[4] has been applied to study the electron transfer process between donor and acceptor states, though the model used a work function model to explain the observed charge transfer, and did not explicitly include the concept of bidirectional charge transfer.

This paper provides an initial integration of the surface states model, the bidirectional acid-base model, and computer modeling of donor and acceptor states, and provides both a qualitative and quantitative link between all these disparate aspects.

Experimental

Perdew's 91 generalized gradient approximation (PW91PW91) was employed as the density functional method for QM calculations, using a double numerical basis set with d-polarization functions (DND).

Charge direction was measured by mixing pairs of powders. Kynar or PMMA were coated onto a 35μm ferrite core and charge of metal oxide additives (Degussa A300, P25 and aluminum oxide C) or 3 μm PTFE was measured by blow-off. A large PTFE particle was also utilized as a "carrier" particle in a similar way, measuring charge by blow-off of the metal oxide particles.

Results and Discussion

Charge transfer complexes: density functional theory QM modeling

In the surface states model[1], the difference in chemical potential between insulator surfaces in contact drives the charge transfer, balanced against the surface chemical potential difference. When the two fields match, charge transfer stops. Previous work[2,3] showed that the chemical potential difference arises from a bidirectional charge transfer, both from Lewis base donor sites on surface A to Lewis acid acceptor sites on surface B, and donor sites on surface B to acceptor sites on surface A. The net charge transfer is thus dependent on the difference in energy between these two different charge transfer processes.

A missing link was to identify the actual donor and acceptor sites that are responsible for the charging process. Nikitina[4] used *ab initio* DFT and time dependant DFT to study the charge transfer event between PTFE and metal oxides. Briefly, they calculated the lowest energy configuration of the PTFE-oxide charge transfer pair, along with the associated HOMO and LUMO energies and the work function, through to a non-equilibrium excited state, then used TDDFT to an equilibrated final state, where they calculated partial electron densities transferred in the complexes, which they then related to charge exchange and the triboelectric series, though there was no actual comparison to any specific charging data.

In the current work we use density functional theory (DFT) quantum mechanical (QM) modeling to further developer this idea of the charge pair that developers on contact. The approach in this study is similar in some ways to Nikitina, but focuses on what we call the precursor charge transfer complex that develops when materials come into contact, the complex that enables the charge transfer event. We also explore some of the assumptions made in that study and attempt to fit the QM modeling within the framework of both the bidirectional acid-base charging model, and with triboelectric charge, both qualitatively and quantitatively.

In the first step, HOMO and LUMO frontier molecular orbitals are calculated for isolated PMMA and oxide molecules, the example with silica is shown in Fig. 1. The HOMO would be expected be the donor of the electrons for transfer, while the LUMO would be expected to be the acceptor. Since we will show later that silica accepts charge from PMMA, then the HOMO on the carbonyl group in PMMA is expected to be the electron donor site and the LUMO on the hydroxyl group in silica is expected to be the acceptor site.

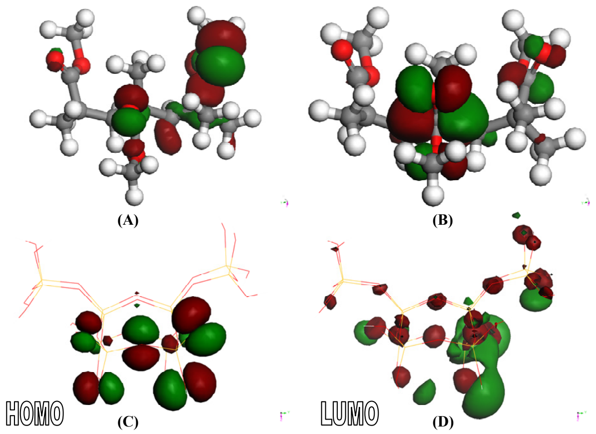


Figure 1. HOMO and LUMO for isolated clusters: A) PMMA cluster HOMO B) PMMA cluster LUMO, C) silica cluster HOMO, D) silica cluster LUMO

Charge transfer occurs with a collision of two surfaces which must provide sufficient energy to enable transfer.[5] In general these collisions will be at random orientations and are energetic compared to conformational energies. Thus preferred orientations in collisions should only be those built into the surfaces, such as surface OH groups on metal oxides. There is no reason to assume the lowest energy conformation is the lowest energy for charge transfer, an assumption Nikitina[4] apparently makes. Our DFT calculations show that two key orientations of the precursor charge complex, the complex that leads to the charge event, are important: those where the polymer dipole either points away from or toward the oxide. For both orientations, energy was minimized and the LUMO and HOMO calculated. Only the precursor complex that leads to charge transfer was studied, not charge transfer itself.

The bidirectional charge model[2] shows charge can transfer in either direction on contact, but was not explicitly studied by Nikitina.[4] The dominant orientation for electron charge transfer, from PMMA to silica--known from experiment--is shown in Fig. 2, and denoted as the forward direction. It corresponds to the carbonyl dipole pointing *away* from the silica. Charge transfer in the reverse direction has a larger energy gap, and thus is less favorable, although it still occurs and is important. The HOMO and LUMO MO's for the PMMA-silica complex are shown in Fig. 2. As with the isolated molecules, the HOMO is located on the PMMA, the LUMO on silica—so charge is donated from PMMA to silica, resulting in the negative charge on silica.

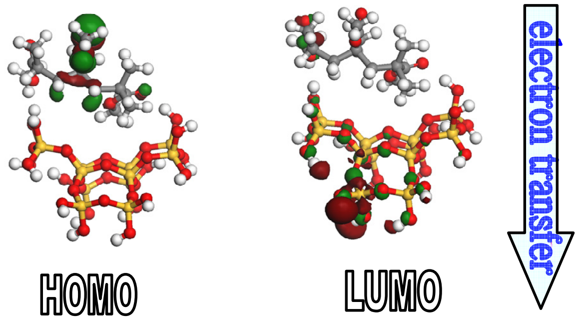


Figure 2. PMMA-silica complex with alkyl groups of PMMA facing silica hydroxyls showing forward charge transfer and HOMO and LUMO's.

The relationship between the energy level diagram for the molecular orbitals in isolated molecules and the charge transfer complex are shown in Fig. 3. Note that the HOMO to LUMO energy gap is changed only slightly between isolated molecules and the complex, due to intermolecular orbital overlap. While it is not known if this small change in LUMO and HOMO energy levels is general, a self-consistent triboelectric series depends on this difference being small. If it were large then the position of a material in the series could change depending on the pairing of materials and no general tribo series could exist. On the other hand, specific pair-wise interactions could explain why sometimes material pairs do not behave as expected based on the triboelectric series in some cases. Though of course, such things as surface contamination and impurities and physical materials transfer can also alter results from the expected tribo series.

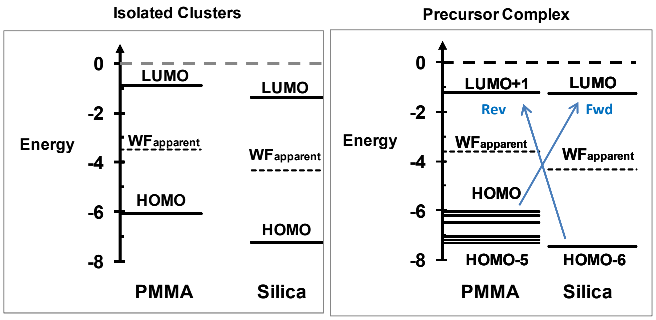
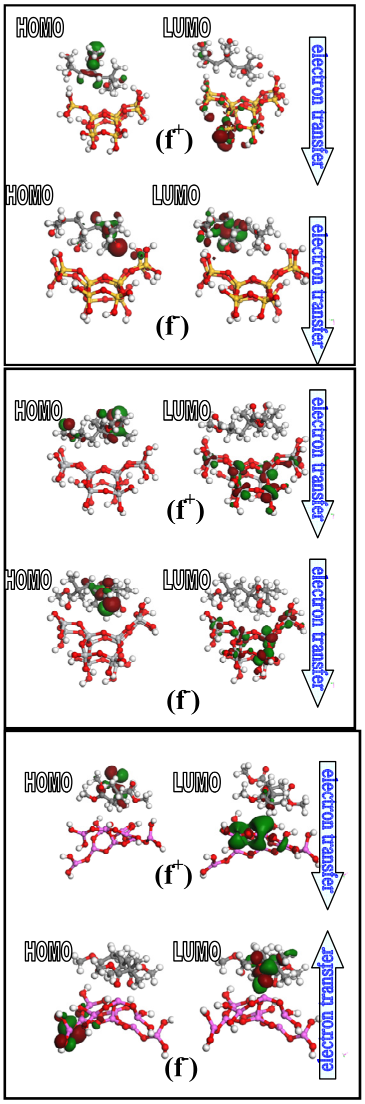


Figure 3. Energy level diagram for molecular orbitals, and relationship to Lewis acid-base parameters for: a) isolated PMMA and silica and b) PMMA-silica charge transfer complex. Excited states are not show for the isolated case.

As mentioned above, two different orientations have been found to be generally useful in understanding the charge transfer properties, one where the carbonyl group faces the oxide, and one where the carbonyl group faces away and the polymer alkyl groups face the oxide. The HOMO and LUMO of charge transfer complexes for different oxides with PMMA are shown in Fig. 4. Here we introduce the concept of Fukui functions, which are the key indicators for regioselectivity in electron-transfer dominated reactions. We use them to predict the electrophilic (f^-) and nucleophilic (f^+) maxima of PMMA, the molecular locations of electron donation and acceptance, respectively. The f^+ orientation of PMMA thus has the nucleophilic side facing the silica (the methylene alkyl groups), while f^- has the electrophilic side of the PMMA cluster, the carbonyl groups, facing the silica. Fig. 4 shows both orientations of PMMA with silica, alumina and titania. In all cases, the f^+ orientation results in the lowest electron transfer gap from the PMMA to the oxide. For the f^- orientation, the energy gap is slightly favored for transfer to silica, strongly favored for titania, while for alumina, electron transfer to PMMA is favored. Thus, the prediction in terms of energy gaps is that silica and titania will charge negative, as observed, while with alumina each charging direction is favored in one orientation. Thus, for alumina the two charging processes will tend to counterbalance, and provided the occurrence of these two orientations in surface collisions is similar, we predict alumina will not charge well with respect to PMMA, as observed.



	Silica		Titania		Alumina	
PMMA Orientation	f^+	f^-	f^+	f^-	f^+	f^-
Charge Transfer To Oxide (eV)	4.61	5.38	2.67	2.89	3.74	4.68
To PMMA (eV)	6.23	5.48	>4.16	>4.21	5.65	3.78

Figure 4. Active electron transfer sites and orientation dependence for silica, titania and alumina vs. PMMA.

Linking QM Modeling to Acid-Base Parameters, Contact Potentials and Triboelectric Charging

In the bidirectional charge model we must consider charge transfer in both directions to fully understand charge transfer, as all materials have both electron donation and acceptance capability, characterized by a base parameter, K_b, and by an acid parameter, K_a, respectively. For two surfaces A and B, the energy gap for charge transfer from A to B is proportional to log $[K_b(A) \bullet K_a(B)]$, while the energy gap for electron transfer from B to A is proportional to log $[K_b(B)/K_a(A)]$.[2] Thus, the *apparent* work function difference, or contact potential difference (CPD), for insulators is described by Eq. (1), the average of the forward and reverse charge transfer processes between discrete acid and base sites on the two materials. Here C is a constant.

$$\mathrm{CPD}(A,B) = C \bullet \log [K_b(A)/K_a(B)] - \log [K_b(A)/K_a(B)] \quad (1)$$

In previous work[3,6] oxide contact potentials were correlated strongly to K_a/K_b values. From that correlation, and published K_a and K_b values, it is possible to predict the CPD values. Fig. 5 shows CPD values referenced to polystyrene. There are few CPD measurements in the literature for polymers that have measured K_a/K_b values. Yanagida[7] measured work functions at 40% RH by CPD and by UV photoelectron spectroscopy. CPD and K_a/K_b values from ref. 6, which were measured as a function of RH, were interpolated to 40% RH to compare to Yanagida. The correlation shown in Fig. 5 is reasonable, although data is limited.

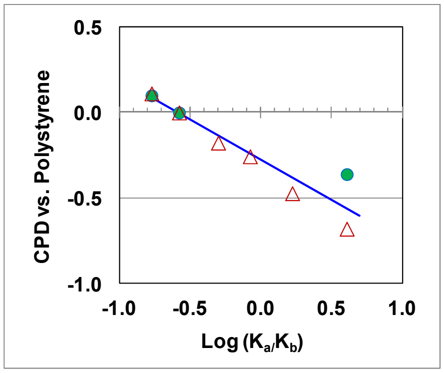


Figure 5. Relationship of chemical potentials to surface acid-base parameters: △calculated from K_a/K_b and CPD data[6], ● measured[7]

Fig. 6 shows the predicted direction of charge exchange using DTF to calculate the precursor energy levels, as shown for example in Fig. 3 and 4, then comparing the energy gaps to determine the lower energy forward charge transfer direction. The DFT predictions were compared to that measured by mixing powders for tribo blow-off. Here we are *qualitatively* predicting the triboelectric series. The direction of charge exchange is predicted correctly for oxides charging with PMMA. Alumina and silica are predicted correctly for charging with Kynar, but titania is predicted to be negative, while no charge exchange was observed. However, titania is predicted to be to the negative side compared to alumina in the kynar series, the observed order. For charging with PTFE, alumina is predicted to be positive as observed, but silica is also predicted to be positive, while observed charge is negative. Interestingly, the K_a/K_b values predict silica to be positive, in agreement with the modeling, so here the observed charge seems odd. PTFE is a difficult material to measure experimentally, as it is very prone to material physical transfer[8] due to its softness, so experimental measurements could be questionable. For titania, with 11 excited states no charge transfer was seen, though higher states might provide transfer opportunities. Accuracy suffers too much however to calculate these states. Overall there is some reasonable qualitative agreement between modeling and the observed triboelectric series, though more work is needed.

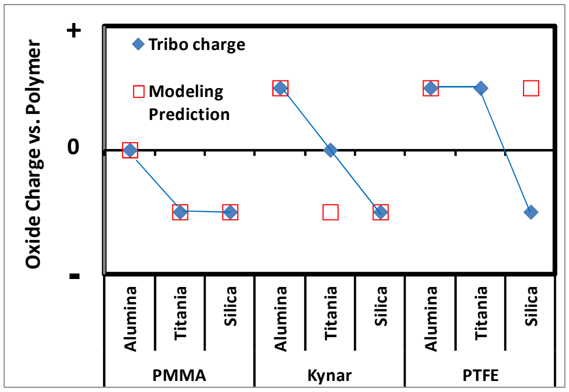


Figure 6. Prediction of direction of charge transfer from DFT modeling and from triboelectric charging

To build a quantitative model, Fig. 7 shows a linear correlation between the DFT calculated energy gaps, taking the energy gap difference for the polymer as the donor compared to the polymer as the acceptor in the complex, a plot of Eq. 1. So PMMA has a lower energy gap as the donor in the complex. Thus the silica has a negative contact potential difference compared to PMMA. Similarly PTFE has a higher energy gap when the donor, so CPD of the oxides is positive. The correlation also passes close to the origin as it should, although the the slope is not 1:1. Nonetheless a very encouraging start to developing a quantitative model.

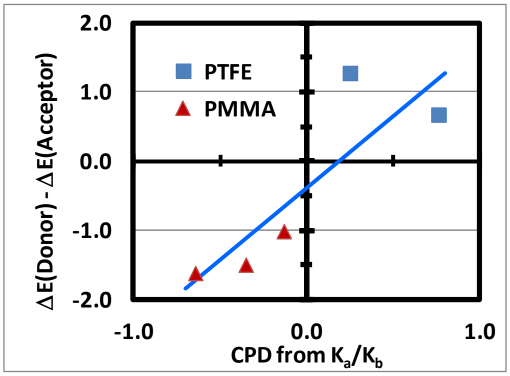


Figure 7. Energy gaps in precursor complex with the polymer as the donor or acceptor compared to CPD of silica, alumina, titania with PMMA and PTFE.

Fig. 8 shows another test of the quantitative DFT model, here the individual energy gaps between the donor and acceptor are shown compared to log (K_a•K_b). Since the charge model is bidirectional, the polymer can be either a donor or an acceptor. Again the correlation is reasonable, and does indeed show that the energy gaps between the donor and acceptor follow the expected trend, the larger K_a (the better the acceptor) and K_b (the better the donor) the smaller the energy gap. In Fig. 8, PTFE as a donor appears to be showing more variation. PTFE is an excellent acceptor, but a terrible donor, so it may be the difficulty is in predicting the very weak donation capacity.

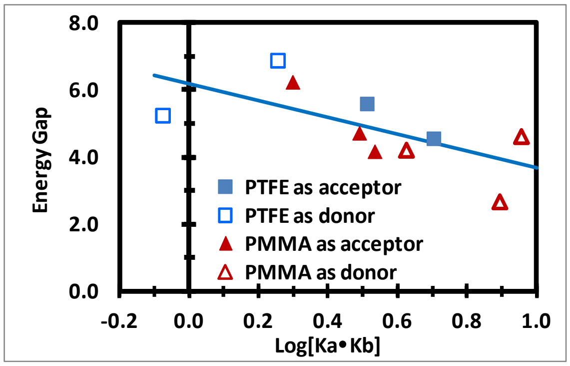


Figure 8. Energy gaps in precursor complex to triboelectric charging of silica, alumina, titania vs. PMMA for forward and reverse gaps

Conclusions

An initial integration of the physics of electron transfer, the surface states model and DFT computer modeling, and the chemistry, the bidirectional acid-base model, is promising. DFT modeling of a precursor complex in the contact of the two charging surfaces, prior to the charge transfer event, provides both a qualitative and quantitative link between all these disparate aspects, for the polymers and metal oxides studied. The importance of different orientations of the polymer dipole in its approach to the metal oxide is also demonstrated.

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Author Biography

Rick Veregin has a Ph.D. in Chemistry from the University of Guelph. For the last 27 years he has worked at the Xerox Research Centre of Canada, as an individual contributor, a manager, and currently as Principal Scientist, Devices & Materials Integration, focusing on the chemistry and physics of xerographic materials and their integration into printing systems. Rick is a member of the IS&T and ACS, and is an IS&T Fellow. Rick has 57 refereed scientific publications and 108 US patents.