INTERFACIAL SPACE CHARGE AND CAPACITANCE J. R. Macdonald, D. R. Franceschetti, and A. P. Lehnen University of North Carolina, Chapel Hill, N.C. 27514, Memphis State University, Memphis, Tenn. 38152, University of North Carolina, Chapel Hill, N.C. 27514

This paper deals with the situation of a single completely blocking electrode at x=0 and an ohmic (infinite surface recombination rate) electrode at $x=\infty$ or at x=&. Some consideration will also be given to theoretical large-signal results obtained when a firstorder reaction occurs at the x=0 electrode (1,2). Thus, only equilibrium or steady-state ionic space charge effects will be considered.

A lattice gas treatment (3,4) of the space charge in a single crystal is appropriate when the charged defect concentration is not negligible compared to the concentration of atom'or anion or cation sites in the crystal. This condition may be present in a superionic conductor, where the undisturbed bulk charge concentration can be very high, or it can occur in the interface-diffuse-double-layer region of a material such as an ionic single crystal when an appreciable potential difference is applied across the electrodes. The usual lattice gas activity takes some account of the finite size of the charge carriers and of the entropy associated with the modes of occupancy of the lattice sites but ignores any further interaction between elements of the "gas," i.e. the charge carriers.

It will be shown how the lattice gas activity can be modified by a type of Frumkin correction to account approximately for the repulsion between charges of the same sign. This modified activity may then be used in equations for the current of the individual charge carriers to yield equilibrium or steady-state space charge distributions, and, in the latter case, current-voltage response. This is still a continuum treatment, but it provides an improved account of the diffuse double layer in solids over that of the traditional Gouy-Chapman (ideal gas) theory. The approach may also be of value for the diffuse space charge in liquid electrolytes since no closed form for the activity of charged hard spheres is known. For a liquid, the modified lattice gas activity becomes more and more appropriate the larger the charge density and also goes to the correct limiting result, the ideal gas, in the limit of low charge concentration.

Results for diffuse double layer space charge distributions and differential capacitance <u>vs</u> applied p.d. will be compared in the case of complete blocking for ideal gas, lattice gas, and modified lattice gas models. Very substantial differences between the ideal gas and the other treatments appear within the range of reasonable applied p.d.'s. In particular, the diffuse double layer capacitance reaches a maximum which is virtually independent of bulk concentration as the p.d. increases, and it decreases slowly thereafter. Some differential capacitance results will also be presented, using the lattice gas activity, which demonstrate the substantial changes which occur as L \equiv ℓ/L_D is decreased from ∞ to 1 to <1 (thin membrane situation), where L_D is here the bulk Debye length. It will also be shown that the lattice gas activity approach is appropriate in two as well as three

dimensions to describe the "adsorption" of Ag^+ ions at kink sites on the surface of single crystal AgCl (4). This approach is entirely consistent with a detailed free energy minimization treatment of such adsorption problems with or without an electrode present. In the former case, results will be presented which take consistent account of the presence of inner layer capacitances, more accurate diffuse double layer capacitance, and adsorption capacitance. A new equivalent circuit for such a system will be presented. An important result of the treatment is that the peak of the adsorption differential capacitance curve <u>vs</u> applied p.d. does not generally occur at either zero applied p.d. or at zero diffuse double layer charge (flat-band). In addition, the maximum observable capacitance is not limited by the magnitude of the diffuse double layer capacitance and may be much larger than the latter.

The continuum lattice gas treatment of space charge in single crystals can be improved, we believe, by treating each crystal plane parallel to the electrodes as an individual adsorber of charge, described by the two-dimensional lattice gas (or modified lattice gas) activity. One finds that the charge in each plane is determined by a Langmuir adsorption isotherm (with a Frumkin correction in the case of the modified lattice gas assumption). The potential between each plane varies linearly with x in this model, and the model can be solved completely and self-consistently using simple electrostatics and a potential-dependent adsorption isotherm at each plane. Such a treatment avoids the well-known difficulties of a fully discrete N-charged-body problem, can take some account of lattice sites, ion size, and charge repulsion within planes, but treats interplanar interactions by an averaged approach. We shall demonstrate the very substantial differences between the space charge distributions and differential capacitance vs applied p.d. for this semi-discrete model and those of the continuum lattice gas model found when the separation between each charge plane includes one or more Debye lenghts.

INTERCATIVOE INSTRUCTION

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DISCUSSION

RICHARD P. BUCK (University of North Carolina): (1) How is the lattice site parameter N related to real parameters (such as ion concentration and ion size) for the diffuse theory? (2) How do the adsorption saturation (or near saturation) results for capacitance contrast with prior results of Grimley and Grimley & Mott?

J. ROSS MACDONALD: (1) The parameter N measures the concentration of sites where positive or negative charges can reside. In a Schottky defect single crystal such as NaCl, for example, N is equal to the underlying concentration of Na⁺ or Cl⁻ ions in the pure crystal. In a liquid, N can be no larger than the value following from close packing of charges of a given sign. For simplicity in applying our work to liquids we took the sizes of positive and negative charge carriers as equal. (2) Although it appears that Grimley was the first to calculate and apply the lattice gas model for both liquids and single crystals, he only calculated space charge and did not consider differential capacitance. Thus he did not discover that the capacitance reaches a maximum which is virtually independent of bulk concentration, an important result of our work.