



Analysis of the Kinetics of Electrochemical Migration on Printed Circuit Boards Using Nernst-Planck Transport Equation



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ABSTRACT

Electrochemical migration can occur on printed circuit boards when exposed to moisture or condensed water drops, thus causing dendrite electrodeposits, which can give rise to short circuits. This study used the Nernst Planck equation and impedance measurements to model the kinetics of electrochemical migration under condensed water drops between copper conductors on printed circuit boards. The time needed for an embryonic dendrite to appear at the cathode and for it to grow from cathode to anode was calculated by the model and confirmed experimentally. It was found that by determining the electroactive ion surface concentration at the anode with the help of impedance measurement, and by considering migration and diffusion in the bulk ion transport, the model matched the experimental results quantitatively. The model was also extended to non-condensing conditions by comparing the conductances in bulk water and moisture films. Historical models were applied to the experimental results and compared with the model of this study.

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1. Introduction

With the trend towards miniaturization and high density in electronics, an electrochemical phenomenon known as electrochemical migration (ECM) can occur on printed circuit boards (PCBs) when PCBs are exposed to moisture or condensed water drops with applied potential difference. ECM is divided into a few steps: path formation, electrodisolution, ion transport, and electrodeposition [1]. Path formation refers to the adsorption of a continuous moisture film on the surface of substrates as a leakage path under non-condensing conditions. (Under a condensing condition, such as a water drop bridging the gaps between metallizations, the path formation step is not required.) After path formation, metal from the anode, under an electric field, dissolves into the electrolyte, migrates through the electrolyte, and deposits on the cathode in a neutral form. Thus, dendrites form and grow from the cathode toward the anode, which is the manifestation of electrodeposition on a macroscopic level.

Because dendrite growth can lead to the degradation of surface insulation resistance (SIR) and even short circuits when dendrites extend to the anode, ECM constitutes one failure mechanism in

electronic products. The propensity for ECM is exacerbated when products are designed to be smaller in that compacted designs shrink conductor spacings and increase the electrical field. Due to its disadvantageous effect, the modeling of time to failure (TTF) caused by ECM is of special interest in electronics.

Barton and Bockris [2] provided the first quantitative model to describe dendrite growth speed with respect to overpotential and radius of growth tip. An optimum growth speed was derived based on the variation of tip radius. The growth speed was observed to be constant and have a linear or parabolic relation to overpotential depending on whether the exchange current approaches zero or infinity, respectively. The time from application of bias to initiation of embryonic dendrites, known as incubation time, was extrapolated by the length of dendrites after they grew. However, this method cannot be used to predict incubation time and cannot explain the physics in this period.

Despic et al. [3,4] extended the Barton and Bockris theory to the current density in the nonlinear region under activation and diffusion control, and considered the multi-step electron discharge process. Diggle et al. [5] developed a model to extrapolate the incubation time based on the initiation of zinc dendrites from the rotation of screw dislocations, but this model had only a qualitative match with the experimental results, especially when zincate concentration approached a dilute solution. The propagation rate, assuming an activation control in the growth process, had a good match with experimental results.

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Popov et al. [6–8] extended the model for incubation time as a function of overpotential, bulk concentration, and initial height of protrusion based on the exponential dependence of surface roughening amplification on time in the dendrite initiation process. It was found that, after a certain limit, the incubation time had no dependence on overpotential anymore.

Shyu [9] developed a model by considering ion transport (diffusion control only), activation, and surface energy using interfacial instability and perturbation theory to describe the incubation and growth process. This model was able to determine the critical overpotential as a function of exchange current density and the growth rate by assuming the tip radius to have a paraboloid shape. However, the incubation time could not be quantitatively determined, and the fitting between the growth model and the experimental results from Diggle [5] probably has to be improved due to the difficulty of measuring the exchange current density at that time.

Previous researchers [2–9] have always used a supporting electrolyte such as KNO_3 , $NaNO_3$ or others in the study of the ion deposition process. More recently, the study of dendrite growth and its morphology with an unsupported binary electrolyte such as $CuSO_4$ or $ZnSO_4$ has attracted much attention due to its tendency to produce dendrites instead of fractals in a much more efficient way [10–23]. By considering diffusion and migration, Chazalviel [10] showed analytically and numerically the existence of a space charge region in the vicinity of the cathode due to the depletion of anions. A characteristic time (Sand time) for building up this space charge region can be an explanation of incubation and is probably close to incubation time. The dendrite growth speed is equal to the velocity of anions, and is proportional to anion mobility and electrical field in the neutral region. The pinpointing of space charge constituted a milestone finding in this field. The growth rate was confirmed experimentally by Fleury et al. [11] in copper sulfate and copper acetate electrolytes, but not confirmed by Devos [12] in copper sulfate electrolyte added by oxalate ions.

Fleury et al. [13–16] investigated the role of convection in the dendrite growth process and found that the space charge created electro-convective motions in the vicinity of dendrites, forming contra-rotative vortices between neighboring branches. With the increase of convection, the space charge size decreases. In a higher concentration binary electrolyte, the gravity-induced convection may also play a role [17], probably down to a $70\ \mu\text{m}$ -thick cell [18]. Marshall et al. [19–23] simulated the dendrite growth process using the Nernst Planck equation (ion transport), Poisson equation (potential profile), and Navier-Stokes equation (hydrodynamic flow); they demonstrated the evolution of gravity-induced convective tube and electro-convective rings, qualitatively matching the experimental results. These studies [13–23] have provided deep insight into the role of convection in this process.

By assuming migration control in the incubation period, Bradley [24] concluded that incubation time in spatially coupled bipolar electrodes (SCBE) is proportional to the gap distance between electrodes and the inverse of cation mobilities and an electrical field. This was simulated by Marshall [25] in electrochemical deposition (ECD) and SCBE and provided qualitative agreement with experimental results. These studies, together with Chazalviel and Fleury's work, clarified the role of cation mobility in the incubation period and anion mobility in the growth period. The orientation of cells was also studied. A vertical cell is more likely to stabilize the electrochemical system than a horizontal cell [26].

These studies have provided a strong background about dendrite initiation and growth, but there exist three differences between ECD in electrochemistry and ECM on electronics, which may limit the application of these theories to ECM. First, the ion transport medium on electronics is an adsorbed moisture film, or bulk water resulting from condensation during thermal cycling conditions (power on and power off, transition from a hot

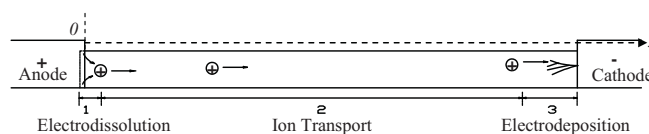


Fig. 1. Steps of transportation process for ECM under deionized water.

environment to a cold environment, etc.). The thickness of ion transport media may constrict the influence of convection. Second, the ionic strength in the medium is relatively low in ECM compared to ECD solutions that contain electroactive ions and possibly supporting electrolyte. Third, the electroactive ions (Cu^{2+} , Zn^{2+} , etc.) are readily available for deposition in ECD, while there are no electroactive ions in the transport media prior to the application of potential difference in ECM.

DiGiacomo [27] developed a model to consider the chances of condensation on substrate surfaces and describe the TTF as the ratio of circuit physical parameters to environmental stress conditions (temperature, humidity, and potential difference). This model assumed that dendritic growth is migration-controlled and predicted that the TTF is proportional to the inverse of voltage or square of voltage depending on the curve fitting of the experimental results. Yang et al. [28] developed an overall regression model using environmental stress conditions. However, there is a lack of physicochemical models that can explain the physical processes and be used to predict the TTF of ECM on electronics.

This study focuses on adjusting the theories on ECD and applying them to ECM under condensed conditions. Then the model developed is extended to non-condensing conditions. Electrochemical impedance spectroscopy (EIS) is used to obtain charge transfer resistance R_{ct} , which helps to calculate the surface concentration of electro-active ions at the anode. The Nernst Planck equation is used to model the ion transport and calculate the incubation time and growth time. Finally, the previous ECD models are applied to our experimental results and compared with the model in this study.

2. Theoretical Model of Copper Ion Transport Time

Fig. 1 shows the different steps of the ECM process under the deionized water drop test. The TTF is the sum of incubation time and growth time. Incubation time is the time needed to initiate embryonic dendrites, which is the sum of ion dissolution, transport, and deposition time until a critical amount is deposited at the cathode to be detectable. The growth time is the time from the appearance of embryonic dendrites, via the propagation of dendrites, until the bridging of dendrites between the anode and the cathode.

It is assumed that $A_{\gamma_1}B_{\gamma_2}$ is the binary electrolyte with charge numbers z_1, z_2 , respectively. The subscripts γ_1 and γ_2 are the number of atoms in the chemical formula. Based on electroneutrality, $z_1 \cdot \gamma_1 + z_2 \cdot \gamma_2 = 0$. It is assumed that A is electroactive and that B is inert. With deionized (DI) water with no supporting electrolyte and no electroactive ions prior to the application of potential difference, the low concentration of electroactive ions in the cell and thus the low density gradient makes buoyancy-driven convection unlikely, based on [17]. In addition, the experimentally measured electroconvective velocity was found to be much smaller than the predicted value by using the model developed by Fleury and Chazalviel (5 orders of magnitude difference) [29], which suggests that the contribution of electroconvection to the overall transport on the ECM on PCBs is not dominant. So we start with diffusion and migration as an approximation of a real case. Based on the Nernst-Planck equation and assuming that convection does not dominate the process,

$$J_1 = -D_1 \frac{\partial c_1}{\partial x} - \mu_1 c_1 \frac{\partial \phi}{\partial x} \quad (1)$$

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