Exact Solution for Contact and Top-Layer Resistivity in Two-Layer Electrodes: Applications for Li-ion Anodes

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Many experimental configurations have been developed to measure conduction in multilayered structures (1, 2, 3, 4). Recently, we have developed an approximate solution for the first-layer (i.e. active material) conductivity using four-point-probe (5), which has been shown to have applicability in design of anodic materials for Li-ion cells (6). Here we describe a new integral approach allowing exact calculation of the contact resistivity in these materials. The in-line four-point-probe configuration modeled is shown in Fig. 1.
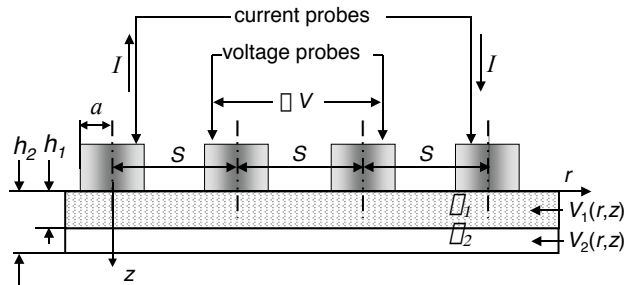

Fig. 1. Schematic of experimental design.

The potential distribution of the multilayered structure is obtained by solving Laplace's equation (Eq. [1]), with potential function defined as V_i, (ith layer) and a single contact area of radius, a, as

$$\frac{\partial^2 V_i}{\partial r^2} + \frac{1}{r}\frac{\partial V_i}{\partial r} + \frac{\partial^2 V_i}{\partial z^2} = 0 \qquad [1]$$

where r and z are the cylindrical axes as shown in Fig. 1. Surface boundary conditions are specified as

$$\frac{\partial V_1(z,r)}{\partial z} = 0 \qquad \text{where } r > a \text{ and } z = 0 \qquad [2]$$

and the current distribution at the interface of first layer with the probe is assumed to have uniform potential distribution (per Schumann and Gardner (4)) as

$$\mathbf{j}(r) = \frac{I}{2\pi a \sqrt{a^2 - r^2}} \quad \text{for } r \le a \text{ and } z = 0 \qquad [3]$$

At interface of the first layer and the second layer, we use the continuity condition

$$\frac{1}{\rho_1}\frac{\partial V_1(z,r)}{\partial z}\bigg|_{z=h_1} = \frac{1}{\rho_2}\frac{\partial V_2(z,r)}{\partial z}\bigg|_{z=h_1}. \qquad [4]$$

Then, the voltage difference between the first and second layers due to contact resistance, p_c, and current intensity, j, can be expressed as

$$V_1(z,r)\big|_{z=h_1} - V_2(z,r)\big|_{z=h_1} = \mathbf{j}\cdot p_c \qquad [5]$$

Finally, we assume no current flow from the bottom of the specimen, per

$$\frac{\partial V_2(z,r)}{\partial z}\bigg|_{z=h_2} = 0. \qquad [6]$$

Solution of these relations results in an integral expression for voltage distribution. Taking the second layer resistivity as known (i.e. resistivity of the copper foil in a Li-ion anode), and varying probe spacing, the resistivity of the first layer and the contact resistance at the interface of the first and second layer is determined. We measured the resistivity of Li-ion anodes (Table I) produced at LBNL, and used the analytical approach to determine resistivities.

Table I. Contact and first-layer resistivities for experimental materials.

Electrode no.	Electrode Condition	Electrode thickness (mm)	Resistivity of 1st layer (µΩcm)	Stdev Resistivity of 1st layer (µΩcm)	contact resistivity (µΩ cm^2)	Stdev contact resistivity (µΩ cm^2)
028-09-4	unpressed	0.1	7.99E+05	2.39E+05	3.24E+05	8.60E+04
028-09-5	pressed	0.09	7.50E+05	2.28E+05	3.87E+05	9.38E+04
028-09-6	pressed	0.085	7.71E+05	1.11E+05	4.93E+05	4.45E+04
028-12-1	unpressed	0.094	1.60E+04	2.40E+03	1.85E+02	9.60E+01
028-12-3	pressed	0.083	1.18E+04	2.11E+04	1.05E+03	1.51E+03
028-12-4	pressed	0.081	1.44E+04	2.35E+04	1.22E+03	1.51E+03
028-12-5	unpressed	0.091	7.91E+04	1.49E+05	1.86E+04	4.48E+04
028-12-6	pressed	0.083	1.49E+05	9.21E+04	1.69E+04	1.04E+04
028-12-7	pressed	0.08	8.73E+04	4.86E+04	1.45E+04	4.20E+03

Conclusions

Results show that there may be an optimum thickness produced by pressing. Interestingly, contact resistance increased with pressing, though material compositions varied in the electrodes; the importance of these distinct effects will be the subject of future study. The experimental/analytical techniques developed here allow measurement of active material resistivity and contact resistivity between the active materials and current collector. These methods may allow development of guidelines for design of superior electrodes by allowing selection of materials which reduce the active material resistivity.

Acknowledgements

References

1. D. H. Dickey, in Spreading Resistance Symposium, National Bureau of Standards Special Publication, **400-10**, p. 45, Proceedings of a Symposium Held at NBS, Gaithersburg. Md (1974).
2. L. J. van der Pauw, Phil. Res. Rep., **13**, 1 (1958).
3. ASTM standard F 673-90.
4. P. A. Schumann Jr. and E. E. Gardner, J. Electrochem. Soc., **116**, 87 (1969).
5. C. W. Wang, K. A. Cook and A. M. Sastry, submitted to J. Electrochem. Soc., (2002).
6. K. Striebel, J. Shim, C.-W. Wang and A.M. Sastry, abstract for The Electrochemical Society 202nd meeting, Salt Lake, UT(2002).