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This Week's Citation Classic

Patterson J W, Bogren E C & Rapp R A. Mixed conduction in $Zr_{0.85}Ca_{0.15}O_{1.85}$ and $Th_{0.85}Y_{0.15}O_{1.925}$ solid electrolytes.
J. Electrochem. Soc. **114**:752-8, 1967.
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The first reported measurements of electronic conduction in oxide solid electrolytes and a useful new method for analyzing data from DC polarization experiments were reported in our paper. [The *SCI*® indicates that this paper has been cited in over 130 publications since 1967, making it the 11th most-cited paper published in this journal.]

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"Long before 1967, zirconia- and thoria-based galvanic cells were known to give reliable high temperature data on free energies and oxygen activities, but only under certain conditions. Theory had established that excessive p-type and n-type electronic conduction could be anticipated under extreme conditions; it was also known that such effects would cause erroneous reductions in galvanic cell EMFs. Cells under very reducing conditions were particularly suspect, but precisely where the trouble should occur was unknown. Hence, when a galvanic EMF came out too low, particularly under reducing conditions, the discrepancy was often attributed to n-type electronic conduction.

"Surprisingly, no one had thought to check this out by actually measuring the electronic conduction in these oxides. The necessary method was not only known but had already been used to measure electronic conductivities in other solid electrolytes, particularly the halides. Rapp, realizing the need for such measurements in the oxides, convinced Eric Bogren and me—the first two in his long list of graduate students—to undertake the task. Just prior to this, Rapp had studied with Wagner in Germany. They had been corresponding on these and other matters since then.

"Certain experimental problems not encountered in the earlier works hampered us severely. Chief among these were the electrode-atmosphere interactions which were almost nonexistent at the much lower temperatures of the previous studies. In the end we finished only two electrolytes, though an array of other compositions had been planned.

"Today one uses closed-tube specimens to block all oxygen gas leakage around the conducting region of the specimen. But this was a first study of the oxides and we did not use tubes. Therefore we could have had residual ionic currents being fed by electrode-to-electrode oxygen leakage via the 'inert' gas atmosphere. This could only cause us to err on the high side, but our results kept coming out *below* the earlier estimates. It is now felt that many of the reduced EMFs on which the earlier estimates were based resulted *not* from electronic conduction but from the formation of 'concentration polarization' layers at the electrode/electrolyte interfaces. Such layers also cause EMF reductions which can be mistakenly attributed to electronic conduction.

"To minimize these and other effects, we had to stay away from the very high and very low P_{O_2} regimes of dominant p-type and n-type conduction respectively. This denied to us the only two methods then available for analyzing DC polarization data. Eventually we devised a third method specifically for intermediate P_{O_2} regimes where neither mode of electronic conduction dominates strongly over the other. With it one can linearize polarization data from such regimes and then extract *both* the p- and n-type conductivities from a single plot. It is cited mainly because it provided the first reported measurements of electronic conduction in oxide solid electrolytes and provided a useful new method for analyzing data from DC polarization, and because electronic conduction severely limits the performance of galvanic cells. It was favorably reviewed by Choudhary *et al.* as recently as 1980.[1]

"Our paper has been referred to in too many review articles over the years to give a representative listing here. Among the more important, however, are those by Rapp and Shores,[2] Etsell and Flengas,[3] myself,[4] Heyne,[5] and Choudhary *et al.*"[1]

1. **Choudhary C B, Maiti H S & Subbarao E C.** Defect structure and transport properties. (Subbarao E C, ed.) *Solid electrolytes and their applications.* New York: Plenum Press, 1980. p. 1-80.
2. **Rapp R A & Shores D A.** Solid electrolyte galvanic cells. (Rapp R A, ed.) *Techniques of metals research. Volume 4, part 2. Physicochemical measurements in metals research.* New York: Interscience. 1970. p. 123-92.
3. **Etsell T H & Flengas S N.** The electrical properties of solid oxide electrolytes. *Chem. Rev.* **70**:339-76, 1970. [The *SCI* indicates that this paper has been cited in over 120 publications since 1970.]
4. **Patterson J W.** Conduction domains for solid electrolytes. *J. Electrochem. Soc.* **118**:1033-9, 1971.
5. **Heyne L.** Electrochemistry of mixed ionic electronic conductors. (Geller S, ed.) *Solid electrolytes.* Berlin: Springer-Verlag, 1977. p. 196.