Proton Injection in the Highly Conducting Mixed Valence Square Planar Platinum Complex; $K_{1.64}Pt(C_2O_4)_2{\cdot}xH_2O$ New Solid State Proton Galvanic Cell

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Summary Single crystals of $K_{1{\cdot}64}Pt(C_2O_4)_2{\cdot}xH_2O$ display non-ohmic behaviour in applied electric fields which is shown to be associated with proton injection at the anode; the half cell reactions associated with this proton migration constitute a new solid state proton battery with cell potential in the range 0·3 to 0·5 V.

The complex $K_{1{\cdot}64}Pt(C_2O_4)_2{\cdot}xH_2O$ is a member of a class of formally mixed-valence square planar complexes containing platinum chains[1] which have recently been shown to possess high electronic conductivity along the metal chain axis.[2-4] The crystals grow as needles from aqueous solution and have a coppery metallic lustre parallel to the metal chain axis (the needle axis). We report that above a critically applied voltage which depends on electrode composition, the conductivity for single crystals of this mixed-valence oxalate displays a non-ohmic behaviour which visually coincides with the formation of a new phase emanating from the anode and travelling toward the cathode. We have interpreted this new phase as caused by the formation of protons at the anode which migrate in the applied electric field across the sample to the cathode.

When an electric field greater than 200 V cm^{-1} is applied across a single crystal of the mixed valence oxalate whose ends have been painted with silver conducting paste, a dark phase whose colour varies from grey-black to greenish-grey appears at the anode and migrates toward the cathode with a sharp front. The speed of migration decreases with time but the front can be made to travel all the way to the cathode in 3 h by increasing the field to 650 V cm^{-1}. The phenomena is not just a surface effect since cross sections of the dark material look uniform throughout. Measurement of the conductivity using a four probe technique shows that the conductivity falls from $1{\cdot}4\ \Omega^{-1}\ cm^{-1}$ to $5{\cdot}9 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ as the dark phase migrates toward the cathode. With the appearance of the dark phase the samples begin to bulge out from between the silver electrodes suggesting that the crystals are expanding along the metal chain axis. On one occasion when the dark phase reached the cathode, small water droplets began to poke through the silver paste cathode and collect in a small puddle. When wet Hydrion pH Paper B was touched to the dark solid phase, a pH of 1 was found whereas the pH of the mixed-valence oxalate before the appearance of the dark phase was 6. On continuing to apply the electric field after the dark phase reached the cathode (at which point the entire sample had a grey-black or greenish-grey colour) the copper phase *reappeared* at the anode after 2 h and migrated toward the cathode although the front separating the two phases was not sharp. With the reappearance of the copper coloured phase, the conductivity began to increase.

We have repeated these experiments with electrodes of aquadag (a colloidal graphite suspension) and with anodes of gelatin impregnated with HCl acidified water and cathodes of silver paste. For aquadag electrodes the electric field necessary to induce the appearance of a new phase is 300 V cm^{-1}; the new phase in this case consists only of a dark narrow band which migrates from the anode to the cathode. On either side of the band the sample is copper coloured. Determination of the current-voltage curve using a four probe technique shows a non-ohmic behaviour above 300V cm^{-1} but ohmic below. In the ohmic region, when a current of 0·036 ma is passed through a sample of dimensions $1\cdot2 \times 0\cdot033 \times 0\cdot033$ mm^3 for 24 h (sufficient to electrolyze more than 500 times its water content) there is no change in conductivity. This indicates that the conductivity in the ohmic region is mainly electronic, not ionic. However, in the non-ohmic region, the four probe conductivity falls from 2·5Ω^{-1}cm^{-1} to 0·097Ω^{-1} cm^{-1} as the dark band migrates toward the cathode. The dark band also has a pH of 1.

For the gelatin anode impregnated with HCl acidified water, the electric field necessary for the appearance of the new phase is less than 20V cm^{-1} with the rate of migration of the new phase increasing rapidly as the gel pH is lowered from 3·4 to 1·6. In this case the new phase can be made to migrate *in the absence of* an externally applied potential simply by shorting out the two ends of the sample. As with the silver paste and aquadag electrodes, the new phase which migrates across the sample has a pH of 1.

The decrease in the electrical conductivity with the appearance of the new phase and the expansion of the crystal along the needle axis suggest that the partially empty d_{z^2} band is filling up. This interpretation is consistent with the expected increase in the metal–metal spacing from 2·85 Å in the mixed-valence oxalate[1] to about 3·2 Å in the non-mixed valence complexes of this class (*e.g.* $CaPt(C_2O_4)_2\cdot xH_2O$, has a Pt–Pt spacing of 3·18 Å).[5] This can be represented as a half cell reaction, equation (1).

$$5\cdot56\text{Pt}^{2\cdot36+}\ (\text{partially empty } d_{z^2} \text{ band}) + 2e \rightarrow 5\cdot56\text{Pt}^{2+}\ (\text{filled } d_{z^2} \text{ band}) \quad (1)$$

The acidity of the new phase, its migration from anode to cathode with the concomitant appearance of water droplets at the cathode suggest that protons are formed as the charge compensating species for the reduction in equation (1). The net effect of the proton injection then would be to change the stoicheiometry of the crystals from $K_{1\cdot64}Pt(C_2O_4)_2\cdot xH_2O$ to $K_{1\cdot64}H_{0\cdot36}Pt(C_2O_4)_2\cdot xH_2O$. Any additional protons which are injected at the anode would be ejected at the cathode by combining with O_2 to form water. While the source of the protons is unknown, the fact that the copper coloured phase reappears after 2 h with silver paste electrodes while only a narrow dark band occurs with aquadag, suggests that the proton source is present in these anode materials in only a small concentration and probably related to the organic binder used in their preparation.

The migration of a new phase from anode to cathode has also been observed for $K_2Pt(CN)_4Br_{0\cdot3}\cdot2\cdot3H_2O$.[6,7] On the basis of *X*-ray analysis and electron microprobe analysis, Gomm and Underhill[6] suggest the half cell of equation (1) is occurring but that Br^- ions migrate to the anode to form neutral bromine as the charge compensating reaction. This process cannot occur in the oxalate complex since there are no anions present. Proton injection and migration is therefore a possible explanation for the new phase in $K_2Pt(CN)_4Br_{0\cdot3}\cdot2\cdot3H_2O$.

The observation that the new phase can migrate spontaneously simply by shorting the ends of the mixed valence crystal when one electrode is gelatin impregnated with HCl acidified water suggests that these mixed valence systems form solid state proton galvanic cells. Indeed, we have found that single crystals of $K_{1\cdot64}Pt(C_2O_4)_2\cdot xH_2O$ and $K_2Pt(CN)_4Br_{0\cdot3}\cdot2\cdot3H_2O$ produce an open circuit potential of 0·33—0·52 V when one end of the crystals is silver paste or aquadag and the other end is gelatin impregnated with HCl acidified water. The water impregnated gelatin is the negative side of the potential. The potential remains constant over a period of 24 h. The same open circuit potential is found for a compressed pellet of the mixed valence oxalate with one face painted with silver paint and the other face covered with a piece of water impregnated filter paper. These results suggest that the insulating non-mixed valence phase which forms at the gelatin electrode acts as a blocking electrode for electron or hole migration but still allows proton transport. In support of this, we have found that when both electrodes are Ag paste, the open circuit potential is zero but becomes 0·11 V when part of the mixed valence crystal is converted to the dark phase. The dark phase is the negative side of the potential. Preliminary current density–voltage studies with the gelatin anode indicate that the battery voltage remains constant for current densities as great as 100 μa cm^{-2}. Further studies on the current density–voltage characteristics of this proton galvanic cell and its current discharge properties with various proton source electrodes are in progress.

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