Semiconductor Electrodes

I. Efficient Electroluminescence at ZnS Electrode in Aqueous Electrolytes

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ABSTRACT

Electroluminescence (EL) on ZnS was studied in aqueous solutions containing various redox species. For species able to generate strongly oxidizing intermediates, such as peroxidesulfate or hydrogen peroxide, bright blue luminescence was observed during cathodic polarization at potentials near to or negative of flatband potential (V_{FB}) of ZnS. For solution containing supporting electrolyte alone or redox couples, no emission was detectable even at potentials 1 V negative of V_{FB}. This suggests that minority carrier (hole) injection is responsible for the initiation of EL. The peak energy of the EL spectrum was much smaller (by 1 eV) than the bandgap of ZnS, suggesting that the radiative recombination is through intermediate luminescent centers. Under steady-state conditions, the EL intensity was proportional to the square of the current, suggesting that EL intensity is dominated by the recombination of electron hole pairs at luminescent centers. In the early part of a potential pulse (especially the first pulse), the growth behavior of EL intensity was strongly affected by the electron trapping of the empty upper luminescent states. The location of the EL spectra depended on the current density and EL intensity; with increasing EL intensity, a significant blue shift of the emission peak was observed. These results suggest that the overall radiative recombination rate might be limited by electron transfer (through a tunneling mechanism) from the occupied upper luminescent states to the empty lower luminescent states. An EL efficiency of 0.2% can be achieved by operating at a current density of 25 mA/cm².

The study of interfacial charge transfer processes at semiconductor electrodes is under active investigation (1-5). Luminescence techniques have been employed successfully as probes to study surface recombination and excited state processes (6-9). Recently Ellis et al. (6) have carried out extensive studies on the electroluminescence and photoluminescence of cadmium chalcogenides, for example CdS and CdSe, and, by comparison with photogenerated charge transfer obtained information about the reaction processes at these electrodes. The efficiency of the room temperature emission of these materials in the visible spectral region is quite low, as is that of most other semiconductors (e.g. quantum yields < 10⁻³).

Wide bandgap II-VI compounds are potentially useful electrode materials for visible electroluminescence in solution; the zinc chalcogenides are especially good candidates for such applications. Indeed, low voltage solid-state devices which produce electroluminescence have been described; however, it is difficult to produce a good p-n junction necessary for efficient charge injection due to self-compensation by native defects. Less complex Schottky junctions have been attempted with some degree of success (10-12). There have been few reports of solution studies of electroluminescence of ZnS (13, 14). In an early letter (14), emission was reported for a ZnS electrode immersed in fuming sulfuric acid; this was attributed to the formation of an inversion layer at ZnS surface. More recently a brief report by Tyagai et al. (13) described the blue emission of a ZnS cathode in H₂O₂, which was attributed to hole injection from the reduction intermediate, OH⁻, into the valence band of ZnS. However, details of the process, the mechanism of emission, and the dependence of the spectral distribution on a variety of electrochemical parameters were not explored. The authors thought it of interest to examine the electroluminescence of ZnS as a probe of the energetics at the ZnS/electrolyte interface and for possible application to display devices.

In this paper, the authors examine the electrochemical and electroluminescent properties of single-crystal n-type ZnS electrodes with various redox couples. They demonstrate that the electroluminescence (EL) is initiated by hole injection from solution redox couples and under steady-state conditions, the EL intensity is dominated by the recombination of electron hole pairs at luminescent centers. Neither electron transfer to the upper states nor hole transfer to the lower states controls the rate of emission in the condition studied. The effect of trapping on the growth of EL and the factors affecting the intensity and spectral distribution of the EL are discussed. The EL efficiency at room temperature is among one of the highest in the photoelectrochemical-type luminescent cells or low voltage solid-state electroluminescence devices (22). An EL efficiency of 0.2% can be achieved by operating at a current density of 25 mA/cm².

Experimental Section

Materials.—Al-doped ZnS single crystals were generously donated by J. O. McCaldin or were grown by iodine chemical vapor transport (15). These crystals usually had high resistivities (> 10¹⁰ Ω-cm). The crystals were heated in a molten 90% Zn-10% Al mixture at 900°C for 10-24 hr. This treatment reduced the resistivity of some crystals to 20-10¹² Ω-cm. The crystals with the highest resistivities were used in the EL experiments. They were cut into slices along the (111) plane and were subsequently polished with carborundum (1 μm grit size) and alumina (0.5 μm particle size). Ohmic contact was made according to the method given by Kaufman and Dowber (16). The crystals were mounted as electrodes as described previously (17). Before a series of experiments, the electrode was etched in a potassium dichromate-H₂SO₄ cleaning solution at 70°C for 5 min. Reagent grade chemicals were used without further purification. All solutions were prepared with triply distilled water and were deoxygenated, if not otherwise mentioned, for at least 30 min with purified nitrogen before each experiment. These experiments were carried out with the solution under a nitrogen atmosphere.

Electrochemical measurements.—All electrochemical measurements were performed with the same electrochemical cells, apparatus, and procedures as reported previously (17). The impedance measurements were carried out with an aqueous solution containing 1.0M NaClO₄. The pH of the solution was adjusted with HClO₄ or concentrated NaOH (10M). The apparatus and procedures for impedance measurements were based on those reported previously (18).
Two a-c frequencies (100 and 300 Hz) were employed and no significant dispersion was found.

Electroluminescence measurements.—The EL spectra were mainly obtained with a PAR Model 1215 OMA2 optical multichannel analyzer including a silicon intensifier target vidicon detector with a vacuum u.v. scintillator to enhance the u.v. response. This detection system has an essentially flat response in the wavelength range of the ZnS EL spectrum, 350-550 nm. To obtain the EL spectra, the electrode was pulsed between 0.0 V vs. SCE and a given negative potential. The EL signal was detected by synchronizing the OMA detection system with the potential pulses applied to the electrode. Another detection system was constructed based on an Oriel monochromator equipped with gratings blazed at 500 or 1000 nm. The monochromator was interfaced to a highly red-sensitive photomultiplier tube (PMT) (Hamamatsu R928). Signals from the PMT were amplified by a lock-in amplifier and displayed on a Houston Model 2000 X-Y recorder. In the transient experiments, the EL signal was detected by a PMT with attached neutral density filters and a 460 nm bandpass filter. Signals from the PMT were amplified by a current-to-voltage converter and displayed together with the chronocapacitometric curves on a Nicolet Model 1090A digital oscilloscope and then recorded on a Houston Model 2000 X-Y recorder.

The integrated EL efficiency, $\phi_{EL}$, was determined by integrating sphere photometric detection system as described by Itaya and Bard (19) and by Bezman and Faulkner (20).

The total photometric apparatus consisted of an integrating sphere and an EG&G radiometer attached to the viewing port of the sphere. The sensitivity, $S$, of the integrating sphere was calibrated with an He-Ne laser or by a light beam (10 nm bandwidth) obtained from a 450W Xe-lamp and an interference bandpass filter at 460 nm. The calibration factor, $C$, of the EG&G radiometer was obtained by a standard actinometric procedure with a 0.1M ferrioxalate actinometer. The sample cell for EL experiments was inserted into the sphere and was held in position by a standard taper joint attached to the sphere. The electrode was pulsed and the total charge passed was measured with a digital coulometer. The total photon energy emitted was measured by the integrating sphere photometric apparatus. The integrated number of photons can be calculated based on Eq. [1] given in Ref. (19) or approximately

\[ \text{the total number of photons (einstins)} \approx S \times C \times \text{total photon energy (joules)} \text{measured} / F \times \text{photon energy } \lambda_{\text{max}} \]  

in which $F$ is Faraday’s constant and $\lambda_{\text{max}}$ is the wavelength at the peak of EL spectrum. In this equation, the average energy per photon is taken as the photon energy at $\lambda_{\text{max}}$. This is only an approximation since the EL spectra are not narrow enough to be treated as line spectra. However, they are quite symmetric and the half-width is narrow as compared with the photon energy at $\lambda_{\text{max}}$.

Results

Electrochemical behavior.—Flatband potential ($V_{FB}$).—Studies of the capacitance of n-ZnS electrodes were conducted in deaerated aqueous solutions containing 1M NaClO$_4$ at different pH’s. As shown in Fig. 1, a Schottky depletion layer was formed at the surface of ZnS, as indicated by the linear dependence of the reciprocal of the square of the capacitance on the potential (Mott-Schottky plot). $V_{FB}$ of this ZnS electrode was $-1.61$ V vs. SCE at pH 1.95 and shifted about 55 mV negatively per pH unit increment. The uncompensated ionized charge density, found from the slope of the Mott-Schottky plots and the dielectric constant ($\epsilon = 8.3$) (21) was $9.1 \times 10^{11}$ cm$^{-3}$.

Voltammetric behavior.—Cyclic voltammetry studies on n-ZnS were conducted in deaerated 1M NaCl solution at different pH’s. As shown in Fig. 2, in the absence of peroxysulfate at pH 11.4, no appreciable cathodic current was observed at potentials positive of $-2.0$ V vs. SCE (curve a). The introduction of 20 mM K$_2$S$_2$O$_8$ into the solution caused an increase in the cathodic current for potentials negative of $-1.8$ V vs. SCE (curve b). This enhanced cathodic current is apparently due to the reduction of S$_2$O$_8^{2-}$ at the ZnS electrode. When the pH of the solution used in b was decreased to 2.2, a diffusion-controlled reduction wave with a peak current, $i_p$, proportional to

![Fig. 1. Mott-Schottky plots of ZnS electrodes in 1M NaClO$_4$ at different pH. A-C frequencies, 100 and 300 Hz. \( \Delta \), pH 1.95; \( \square \), pH 7; \( \bigcirc \), pH 10.](image)

![Fig. 2. Cyclic voltammograms on ZnS electrodes. Scan rate: 100 mV/sec in (a) 1.0M NaClO$_4$, pH 11.4; (b) 1.0M NaClO$_4$, 20 mM K$_2$S$_2$O$_8$, pH 11.4; (c) 1.0M NaClO$_4$, pH 2.3; (d) 1.0M NaClO$_4$, 20 mM K$_2$S$_2$O$_8$ at pH 2.2; (e) 1.0M NaClO$_4$, 20 mM K$_2$S$_2$O$_8$ at pH 2.0. Solution pH was adjusted with concentrated NaOH (10M) and HClO$_4$.](image)
the square root of scan rate and a peak potential, \( E_{p} \), at about \(-1.85 \) V vs. SCE appeared (curve d). This wave can mainly be attributed to proton reduction, because the peak height increases with the proton concentration (cf. curve e with curve d) and the peak position was essentially the same as that corresponding to proton reduction in a solution not containing \( S_2O_8^{2-} \) (see curve c). However the different \( i_p \) values in curves d and c suggest partial contribution by the reduction of peroxydisulfate species. The reduction of \( S_2O_8^{2-} \) does not appear to be strongly pH dependent over the pH range studied. Note that the peak position for \( S_2O_8^{2-} \) reduction of graphite electrodes is essentially pH independent (see Fig. 3).

**Interfacial energy scheme.**—The interfacial energy scheme at the \((ZnS/electrolyte)\) interface at pH 1 is summarized in Fig. 4. The location of the bandedges of ZnS with respect to SCE were calculated based on the procedures reported previously (18) and on the following quantities: the resistivity of the sample, \( \rho = 20 \ \Omega \cdot \text{cm} \); the effective mass of electron, \( m_e^* = 0.34 \ m_0 \) (21) \( (m_0 \) is the mass of free electron); the electron mobility, \( \mu_e = 160 \ \text{cm}^2/\text{Vsec} \) (22); the bandgap, \( E_g = 3.66 \) eV (21, 22) and the flatband potential at pH 1, \( V_{fs} = -1.54 \) V vs. SCE. The conduction bandedge, \( E_c \), was found to be \(-1.74 \) V vs. SCE. This put the valence bandedge, \( E_v \), at a potential of 1.92V vs. SCE. The normal potentials of the \((\text{OH}^-/\text{OH})\) and \(\text{SO}_4^{2-}/\text{SO}_4^{2-}\) couples have been estimated to be 2.7 and 3.2V vs. SCE, respectively (23).

**Electroluminescence (EL).**—Studies of EL from n-ZnS electrodes were conducted in deaerated aqueous solutions containing various redox couples given in Fig. 4 or in oxygen-saturated solution containing no redox couples other than supporting electrolyte, 1M NaClO₄. In the presence of peroxydisulfate or hydrogen peroxide, a bright blue emission was observed starting at potentials negative of \( V_{fb} \) that was readily observable under daylight conditions (Fig. 5). No detectable EL was observed in solution containing only supporting electrolyte even at an applied potential of \(-10 \) V vs. SCE. In Ce(IV) solution, the blue emission was found at potentials far negative of \( V_{fb} \), such as \(-5 \) V vs. SCE. EL with peroxydisulfate was studied most extensively, and details of the results in solutions containing 0.2-1M \( S_2O_8^{2-} \) at different pH's are given below.

**Steady-state current and EL-potential properties.**—As shown in Fig. 6a, the current, \( i \), increases exponentially with potential, and some cathodic current flows when the potential is positive of \( V_{fb} \). This exponential dependence is consistent with the capacitance measurements which indicate the formation of a Schottky depletion layer at the surface of ZnS. When the potential is well negative of \( V_{fb} \), the \( i-V \) characteristic obeys a power law relationship over a wide range of applied potential of the form \( i \propto \sqrt{V} \) with \( n \) equal to 2. This suggests that the current in this potential range is dominated by double injection (24). A current doubling effect is expected with this system based on the interfacial energy scheme shown in Fig. 4.

Different from the \( i-V \) behavior, significant EL intensity is only detected at potentials near to or negative of \( V_{fb} \) (see Fig. 6b), where double injection
Fig. 6. Current-(curve a) and EL intensity-(curve b) vs. potential at ZnS electrodes in 1.0M NaClO₄ and 0.2M (NH₄)₂S₂O₅ at pH 8.4. Scan rate, 20 mV/sec.

takes place. Moreover, the EL intensity rises more steeply, as compared with the current, with increasing negative potential. As shown in Fig. 7, the EL intensity, I, varies according to a relationship of the form $I \propto i^n$, with n equal to 2 over the current range studied.

Spectral distribution.—EL spectra were obtained by repetitively pulsing the electrode between 0.0V and a potential negative of $V_{FB}$. The bright blue emission could be seen easily with the naked eye even under ordinary room light conditions. The EL spectra were obtained by synchronizing the OMA detection system with the potential pulses applied to the electrode.

Since the intensity and the spectral distribution of the EL vary with time during the first several potential pulses and reach a steady-state condition only after some period of cycling, the EL spectra shown were recorded under steady-state potential pulsing conditions, if not otherwise mentioned. The EL growth behavior is described in the following sections.

The EL spectra, shown in Fig. 8, are characterized by a single broad band with maximum EL intensity at about 460 nm. The exact peak position, $\lambda_{max}$, of the EL spectrum depends on several parameters which will be discussed in the following sections. Because the sensitivity of the OMA detection system was low at wavelengths beyond 700 nm, a highly red-sensitive photomultiplier tube (Hamamatsu R928) was used to check the EL spectrum in this region. No other bands were observed out to 1000 nm.

Effects of potential on EL intensity and spectral distribution.—As shown in Fig. 8, significant changes in the intensity and shifts in spectral distribution of the EL were found with small changes of the negative potential limit. More negative step potentials increased the EL intensity and produced a blue shift in the EL spectrum (by about 35 nm in $\lambda_{max}$ with a potential change of $-1.95$ to $-2.25$V vs. SCE). The EL spectrum also was broadened with decreasing negative limits (half-width of 82 nm at $-1.95$V vs. 84 nm at $-2.25$V vs. SCE). Note that the EL spectrum with the higher emission intensity had a sharper high energy edge than that with low emission intensity. This is shown more clearly in Fig. 9 by normalizing curve e in Fig. 7 to the same peak height as curve a and then translating this normalized curve by 35 nm to shorter wavelengths to match the peak positions of the two curves.

Development of electroluminescence and current during sequential potential pulses.—The growth and decay of the EL intensity and current during a sequence of potential pulses between 0 and $-2.75$V vs. SCE is shown in Fig. 10. In the first pulse, the current (the lower curve) reaches a peak value within 5 μsec, which is very close to the rise time of the potential step generated from the potentiostat. After reaching...
EL (≤20 μsec) was much shorter than its rise time. The rise time depended on the history of pulsing and the step potential. Extensive potential pulsing and/or a large amplitude potential step decreased the rise time of EL. A rise time of 200 μsec can be achieved after extensive pulsing of the ZnS electrode between 0 and −3.5V vs. SCE. There was always a dead zone at the beginning of the first potential pulse of a sequence where significant current was observed without generation of a significant amount of EL.

Accompanying the growth of the EL intensity during a sequence of pulses, a blue shift of the EL spectrum was observed. As shown in Fig. 11, the integrated EL intensity during a single pulse increased with pulse number. This is consistent with the result shown in Fig. 10. The integrated EL intensity in the 26th pulse was about 100 times higher than that of the first pulse. Moreover, a pronounced blue shift of about 20 nm in $\lambda_{\text{max}}$ was observed on the EL spectrum of the 26th pulse compared to that of the first.

**Effects of pH on EL intensity and spectral distribution.**—Studies of pH effects on the EL were conducted in deaerated solutions containing 0.2M (NH₄)₂S₂O₈ and 1M NaClO₄. The pH of the solution was adjusted with 10M NaOH and HClO₄. The peak intensity of the EL was a function of pH (Fig. 12). When the potential of the ZnS electrode was pulsed between 0 and −3V vs. SCE with a 5 msec pulse width, the EL intensity reached a maximum value at pH 7–9 and decreased gradually at lower pH and more steeply at higher pH. An increase in pH from 8.0 to 10.1 caused a large decrease in the EL intensity and a red shift of 35 nm in the EL spectrum. Similarly, a decrease of pH from 8.0 to 1.2 decreased the EL intensity and caused a red shift (~18 nm) of the EL spectrum (Fig. 13).
Electroluminescence in the first potential pulse.—The growth of EL during the first pulse was usually very different from that observed under steady-state pulse conditions. The effect of the negative potential limit is shown in Fig. 14. At smaller negative potentials (e.g., positive of −2V vs. SCE), the EL intensity was very low and increased linearly with time (see curve 14a). As the limit was made more negative, the EL intensity increased linearly with time at the very beginning and exponentially approached a saturation value at longer times (see curve 14c), indicating a faster growing-in of EL as compared with that at less negative potentials. A faster rate in EL growth could also be achieved at less negative potentials, if the electrode was prebiased to a potential where no EL was generated but a significant current was observed (for example, a prebias at any potential between −1.4 and −1.8V vs. SCE at pH 8.4).

The effect of prebias on the growth behavior of EL at −2.25V vs. SCE is shown in Fig. 15. Without prebias, the EL intensity was low and grew very slowly (see curve b). The corresponding chronoamperometric curve (curve d) showed a significant current overshoot and sharp decay to a steady-state value. Prebias of the electrode for 30 sec at −1.72V vs. SCE, where no EL but a significant transient current was detected, not only enhanced the EL intensity but also accelerated the growth of EL (see curve a). The current overshoot in curve d disappeared and the current reaches the steady-state value within a few tens of μsec (see curve c).

Efficiency and stability of ZnS electrode.—The EL efficiency was determined in a pulse experiment with a step potential to −2.5V vs. SCE where a steady-state current density of 25 mA/cm² was obtained. An integrated EL efficiency, \( \varphi_{EL} \), was calculated based on Eq. [2]

\[
\varphi_{EL} = \frac{\int_{t_0}^{t_f} \int_{t_0}^{t_f} \text{total light emitted} \times F}{\text{total charge passed through the electrode}}
\]

in which F is Faraday’s constant, the light emitted was in einsteins, and the charge in coulombs. The total light energy, in joules, was converted to einsteins at 460 nm. The broad (FWHM of ~80 nm) but quite symmetric feature of the EL spectrum makes this only an approximation. The EL efficiency at a current density of 25 mA/cm² ranged from 0.2 to 0.35%, depending on the particular electrode. Since the EL intensity depends in a nonlinear way on the current density, as illustrated in Fig. 7, so does \( \varphi_{EL} \). To in-
investigate the stability of the ZnS electrodes in aqueous solution containing peroxydisulfate, the authors performed a long-term pulse experiment. The electrode was immersed in a solution containing 0.2M (NH₄)₂S₂O₈ and 1M (NH₄)₂HPO₄ (pH ~ 8) and was pulsed between 0 and ~2.5V vs. SCE with a pulse width of 5 msec. The EL intensity was monitored occasionally with a radiometer. Since peroxydisulfate is reduced irreversibly on the ZnS electrode and is not regenerated at the counter-electrode, an additional amount of peroxydisulfate was introduced daily into the solution. The pH of the solution was kept at ~8. The EL intensity showed some short-term fluctuation towards more negative values. This favors hole injection into the valence band of n-ZnS. However, efficient hole injection can occur, if a significant net change in potential is observed or a strong negative bias is applied to the electrode so that electron tunneling from the valence band to the solution species can take place. This seems the case for Ce(IV) and Tl(II).

The mechanism proposed for the electroluminescence in S₂O₈²⁻ or H₂O₂ is shown in Scheme I. This scheme has long been applied to explain the edge emission from GaP, CdSe, etc.

![Scheme I](image)

The first stage (Eq. [3]) involves the reduction of S₂O₈²⁻ or H₂O₂ by conduction band electrons of the n-ZnS electrode. This produces SO₄⁻ or -OH; these are sufficiently oxidizing to capture electrons from the valence band in the second stage (Eq. [4]). The radiative recombination of these injected holes with conduction band electrons does not produce edge emission (corresponding to EL) in the present experiment. The peak energy (2.74 eV) of the EL spectrum is substantially smaller than the bandgap (3.66 eV) of ZnS. This subbandgap emission can only be explained based on radiative recombination through intermediate levels, such as the donor impurity level E_D and/or acceptor impurity level E_A.

The interfacial energetics can also be changed by varying the pH of the solution. Capacitance measurements clearly show the strong pH dependence of V_FB of n-ZnS electrodes. Increasing the pH, shifts V_FB towards more negative values. This favors hole injection (Eq. [4] in Scheme I) but makes electron transfer from the conduction band of n-ZnS to solution species (the first step or Eq. [3] in Scheme I) less favorable. Thus at a given potential, the current density and the corresponding EL intensity decrease with an increase in pH. This is consistent with the results shown in Fig. 12 when the pH is beyond 8. The decrease of EL intensity with a decrease in pH at pH < 7 does not fit this argument. The decrease of EL intensity in this pH range might be caused by at least two factors. The first involves the competition between the reduction of proton and S₂O₈²⁻, which produces intermediates that are sufficiently oxidizing to inject holes into the valence band of n-ZnS (see Fig. 4), supports the minority carrier injection mechanism of electroluminescence (6-8, 13). The lack of EL in supporting electrolyte alone and the observation of little EL in solutions containing weakly oxidizing species, such as Fe(CN)₆³⁻, even at a potential far negative of V_FB (for example ~8.0V vs. SCE), rules out the possibility that the energetic holes required for EL are generated by high electric field processes inside the semiconductor, e.g., field-assisted electron tunneling from valence band to conduction band. In solutions containing redox couples with potentials located within the bandgap but close to the valence band of n-ZnS, such as Ce(IV)/Ce(III) and Tl(II)/Tl(I), significant EL was observed only when the n-ZnS electrode was biased at a potential at least 1V negative of V_FB. The requirement of this overpotential is understandable simply based on the energetics for interfacial hole transfer. Both Ce(IV) and Tl(II) are energetically insufficient to inject holes into the valence band of n-ZnS. However, efficient hole injection can occur, if a significant net change in potential is observed or a strong negative bias is applied to the electrode so that electron tunneling from the valence band to the solution species can take place. This seems the case for Ce(IV) and Tl(II).
Spectral distribution and intensity of electroluminescence.—That EL spectra are more asymmetric at high emission intensity than at low intensity as shown in Fig. 9, might be partially due to the effect of self-absorption. If holes can be transferred from some distance into ZnS, the photons emitted there (especially those with shorter wavelength) could be reabsorbed. In contrast, photo-induced electron transfer from traps. Experiments showing a photo-enhanced cathode current and photoquenching of EL, which will be discussed in a separate paper, support this argument. The sharper rise in intensity in the high energy edge is expected from reabsorption of the luminescence by the transition between the band tail (caused by heavily doping) and an initial impurity band states. These results suggest that EL from ZnS is produced in a region extending from the semiconductor/solution interface into a certain depth of the semiconductor. However, due to the much lower (~16 times) hole mobility compared with the electron mobility, the emission zone could be quite thin.

One of the interesting features of the EL spectrum of the ZnS electrode is the blue shift of λ_{max} with increasing excitation rate (current density) and thus EL intensity. Several experimental results have been presented to illustrate this phenomenon. These include (i) the effect of cathodic step potential, (ii) the pH effect, and (iii) the temperature. Assuming that the diffusive component of the current is negligibly small as compared to the drift component, the rate of electron filling of the initially empty lower states. With progressive excitation by a high energy edge of the EL spectrum should be a function of the distribution of states in the low energy region. The high energy edge of the EL spectrum is expected to be a rather abrupt cutoff before the impurity band is completely filled. The experiment does not show this behavior especially at low current densities (low EL intensities).

One of the accepted models to explain this phenomenon is the rate determining step of the EL under steady-state conditions. Neither electron transfer to the upper acceptor levels nor hole transfer to the lower acceptor states controls the rate of emission. This is consistent with the tunneling model discussed above.

At steady state, the electron density of the upper occupied state, n_u, is proportional to exp [e(QFLH)/kT] and the density of free holes, n. The QFLE term represents the quasi-Fermi level of electrons, k is the Boltzmann constant, and T is the absolute temperature. Assuming that the diffusive component of the current is negligible small as compared to the drift component, the current density is thus proportional to N. Hence

\[ \eta_u \propto \frac{1}{i} \]  

The hole density of the lower empty state, p_i, is proportional to exp [e(QFLE)/kT] and the density of free holes, p. The QFLE term represents the quasi-Fermi level of holes, p is proportional to the rate of hole injection which contributes one-half of the total current. The splitting of QFLH and QFLE from the equilibrium Fermi level arises because electrons accumulate in the donor levels and holes accumulate in the lower acceptor states. Thus

\[ p \propto \frac{1}{i} \]  

Since the emission rate is proportional to the product of \( \eta_u \) and \( p_i \), if the radiative recombinational process is the rate determining step, a square law for the intensity-current relationship is predicted.

Effect of trapping on the growth of electroluminescence.—Several experimental results demonstrate the existence of electron trapping, which strongly affects the EL on ZnS. (i) there is a potential region where no EL intensity is detected but significant current is observed (see Fig. 6); (ii) the current overshoots in the first potential pulse, prefacing the electrode or pulsing the electrode continuously eliminates this current overshoot (see Fig. 10 and 15)—this suggests that the current overshoot at the beginning of the first potential pulse is not controlled by solution double layer; (iii) the rate of cathodic limit potential has the same effect on the growth of EL (see Fig. 14).

A simple rate equation is adequate to illustrate qualitatively these points (see Scheme II). If the upper (donor) states are sufficiently deep that the detrapping of electrons to the conduction band can be neglected, the rate of electron filling of the initially
empty upper (donor) states is given by

\[ \frac{dn}{dt} = A_1 n (n_D - n_0) - A_2 n p_1 - A_3 n p_1 \]  
\[ \frac{dp}{dt} \approx 0 \]  
\[ \frac{dP}{dt} \approx 0 \]

in which \( n_0 \) is the density of occupied upper (donor) states, \( n \) the density of electrons in the conduction band, \( n_D \) the total number of upper states (empty and occupied) per unit volume, \( p_1 \) the density of empty lower (acceptor) states, and \( A_1 \) and \( A_2 \) are constants describing the rate of generation of \( n_0 \), the radiative recombination rate and the nonradiative recombination through \( n_0 \) and \( p_1 \), respectively.

The authors assume that before most of the upper states are filled, electron trapping by these states is the predominant process for the consumption of electrons injected from the bulk of semiconductor into the emission zone. Thus, in the early part of the pulse, \( n, p, \) and \( p_1 \) are small and only slowly varying variables, i.e.

\[ \frac{d n}{d t} \approx 0 \]  
\[ \frac{d p}{d t} \approx 0 \]  
\[ \frac{d P}{d t} \approx 0 \]

By integration of Eq. [9] with \( n_0 = 0 \) at \( t = 0 \) and the assumptions in Eq. [10a], [10b], and [10c] yields

\[ n_0 = \text{constant} \]  
\[ n_0 \approx A_1 n p_0 (S/n + A_2 p_1 + A_3 p_1) \]

and

\[ \tau = 1/(A_1 n + A_2 p_1 + A_3 p_1) \]

The EL intensity is given by

\[ I = A_2 n p_1 = A_2 n p_0 \times [1 - \exp(-t/\tau)] \]

This exponential growth of EL was observed at high step potentials and in the time domain away from the beginning of a potential step (Fig. 14).

When \( t/\tau \to 0 \), Eq. [14] reduces to

\[ I = A_2 n p_0 \times t/\tau \]

This linear growth behavior of EL is observed at the beginning of any potential step or throughout the whole width of potential pulse, when its amplitude is small (see curve a of Fig. 14).

The conservation of charges gives

\[ \frac{d n}{d t} + \frac{d n}{d t} - \frac{d p_1}{d t} = i_d \]

with

\[ i_d = i_T - (i_{ch} + i_{ch}) \]

in these equations should represent the current overshoot in the chronoamperograms in the first potential pulses. Combination of Eq. [10a], [10b], [10c], [12], and [18] yields

\[ i_d = (n_0 \times \tau) \exp(-t/\tau) \]

This current transient is clearly shown in the first potential pulse in Fig. 10. The time constant for the increase of EL is very similar to that for the current decay, as expected from Eq. [14] and [18].

The actual mechanism is certainly more complicated than that given above and involves radiativeless recombinations between \( n \) and \( p \), probably via trapping levels. These radiativeless processes are what contribute to the modest efficiency of the observed EL. Additional surface quenching processes by solution species also occur. Such processes are currently under investigation.

Conclusions

Bright blue EL results from the electrochemical reduction of peroxysulfate at an n-ZnS electrode. This luminescence arises from recombination of an electron with a hole injected by an intermediate (SO₄²⁻) in the reduction.

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Electrochemical Reduction of Calcium Chromate

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A saturated solution of CaCrO₄ in LiCl-KCl eutectic is used as the cathode in Ca/CaCrO₄/Fe thermally activated batteries. Upon activation to the molten state, CrO₄²⁻ is reduced at the Fe cathode current collector and Ca is oxidized via a Ca-Li alloy intermediate at the anode (1-4). Since the CrO₄²⁻ solution is in intimate contact with the anode, the CrO₄²⁻ is also reduced at the anode in a side reaction parallel to Ca oxidation. These CrO₄²⁻ reductions at both the cathode and anode produce insoluble product layers which partially control the discharge behavior of the Ca/CaCrO₄/Fe thermal battery (4, 5).

The insoluble chromate reduction product at the anode has been identified by Nissen (4) as primarily Ca₂CrO₄Cl. In partially discharged batteries, Hlava and Headley (6) have identified both Ca₅(CrO₄)₂Cl and Ca₃CrO₄Cl.

Laitinen and co-workers (7-14) have studied extensively the electrochemical reduction of dilute solutions of CrO₄²⁻ in LiCl-KCl eutectic and have observed neither of the above two Cr(V) compounds. By controlled potential coulometry, Ferguson (15) and Bhatia (16) observed that three Faradays of CrO₄²⁻ were required to reduce one mol of CrO₄²⁻ in a single reduction wave. Using chronopotentiometry in the presence and absence of O²⁻, Laitinen and Bankert (7) concluded that this three-electron single-step reduction resulted in the formation of the intermediate CrO₄⁻⁵ which subsequently decomposed to CrO₃⁻³ and O²⁻. Propp and Laitinen (8) examined the reduction of K₂CrO₄ in the presence of Mg²⁺. A nonstoichiometric Cr(III) compound was obtained: Li₂Mg₂CrO₄ (x = 2y = 5). Hanck and Laitinen (10) obtained LiZn₂CrO₄ in the presence of Zn²⁺ and either Ca₂CrO₄ or LiCo₂CrO₄ (depending on specific conditions) in the presence of Co²⁺.

Nezu and Laitinen (11), however, were not able to identify the reduction product of CrO₄²⁻ in the presence of Ca²⁺. Uchida and Laitinen (12) concluded that Ca²⁺ has no effect on the reduction of CrO₄²⁻, and that water associated with hygroscopic CaCl₂ does influence the reduction mechanism and accounts for the irreproducible results of Nezu and Laitinen (11).

By evaluation of the diffusion coefficients and shifts in chronopotentiometric quarter-wave potentials of the CrO₄²⁻ reduction reaction in the presence of divalent metal cations M(II) = Zn²⁺, Mg²⁺, and Ni²⁺, Hanck and Laitinen (10) concluded that CrO₄²⁻ reduction does not proceed in a single-step three-electron reduction reaction to an oxy-anion such as CrO₄⁻⁵ (Laitinen and Bankert (7)) but that it must proceed via an intermediate oxidation state of chromium.

The discovery of Niki and Laitinen (13) that chemically synthesized Li₃CrO₄ is stable in LiCl-KCl eutectic has led Niki, Uchida, and Laitinen (14) to propose that the Cr(V) compound Li₃CrO₄ is a possible intermediate in the electrochemical reduction of CrO₄²⁻ in LiCl-KCl according to the equation

\[ \text{CrO}_4^{2-} + 3\text{Li}^+ + e^- \rightleftharpoons \text{Li}_3\text{CrO}_4 \text{ (solid)} \]  

These authors, however, did not report the synthesis of Li₃CrO₄ by the electrochemical reduction of CrO₄²⁻. The subsequent disproportionation according to Eq. [2] or further reduction according to Eq. [3] of Li₃CrO₄ leads to Li₂CrO₄, the final product in the overall reduction of CrO₄²⁻ in LiCl-KCl eutectic (13, 14).

\[ 3\text{Li}_2\text{CrO}_4 \rightleftharpoons 2\text{Li}_2\text{CrO}_4 + \text{Li}_2\text{CrO}_4 + 2\text{Li}_2\text{O} \]  

\[ \text{Li}_2\text{CrO}_4 + 2e^- \rightleftharpoons \text{Li}_3\text{CrO}_4 \text{ (solid)} + 2\text{O}^{2-} + 2\text{Li}^+ \]

In this report, Li₃CrO₄ has been electrochemically synthesized by reducing CrO₄²⁻ in LiCl-KCl eutectic, thus confirming the hypothesis of Niki, Uchida, and Laitinen (14). The authors have also synthesized Ca₂₃(CrO₄)₂Cl and Ca₃CrO₄Cl by electrochemical reduction of CrO₄²⁻ in the presence of Ca²⁺, Li₂CrO₄, Ca₂₃CrO₄Cl, and Ca₃(CrO₄)₂Cl have each been further...