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14%—Efficiency gallium arsenide photoelectrochemical solar cells

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We have achieved 12–14% AM1 solar conversion efficiencies in n-GaAs |KOH-Na₂Te/Na₂Te_x| graphite redox system using the technique of Ru surface modification, which has been shown to reduce the surface recombination velocity and increase the band bending, resulting in enhanced J_{SC} and V_{OC} . Spectral-response studies were used to determine the effective minority carrier-diffusion length which increased from 0.54 μm to 0.66 μm on surface modification.

THE efficiency and electrical properties of photoelectrochemical (PEC) solar cells depend strongly on the nature of the photoelectrode surface. The surface-modification technique^{1,2} using transition-metal ions has been shown to be a possible method of improving performance and stability of such cells. In this investigation we show that the dark as well as illuminated properties of gallium arsenide (GaAs) photoelectrodes improve considerably, resulting in solar conversion efficiencies between 12% and 14%.

The photoanodes were (100)GaAs, Te doped with $N_d = 4.5 \times 10^{16} \text{ cm}^{-3}$. Surface modification was carried out by matte-etching the polished sample in 1:1 30% H₂O₂:H₂SO₄ and then dipping in 0.01 M hydrated RuCl₃ in 0.1 N HNO₃ for one minute. Ohmic contacts were made by evaporating In–Au (90:10 wt ratio) alloy on the back of the sample, followed by annealing at 450 °C in Ar–H₂ (10:1 volume ratio) for three min. Samples were mounted on a Teflon holder with silicone rubber. After inserting the photoanode, the electrolyte (1 M KOH, 0.1 M Na₂Te/Na₂Te_x) was purged with argon gas for 30 min through a silica gel filter fitted at the bottom of the Perspex electrochemical cell before each experiment.

I – V studies showed a reduction in dark current density J_0 from 0.82 $\mu\text{A cm}^{-2}$ to 0.054 $\mu\text{A cm}^{-2}$ and a decrease in ideality factor n from 3.2 to 1.8 due to Ru surface modification. C–V studies showed corresponding increase in flat-band potential V_{fb} from –1.42 V/Pt to –1.50 V/Pt.

The spectral response was studied using a Jarrell–Ash monochromator whose output was calibrated using a

silicon photodiode. The response curves shown (Figure 1) before and after Ru modification indicated an increase of photocurrent response between $\lambda = (400\text{--}930)\text{nm}$ and reduction of sub-band gap response (inset of Figure 1) as reported earlier^{3,4} for InP and CdTe. The effect of Ru-surface modification is thus to reduce surface recombination velocity thereby improving the effective minority carrier-diffusion length (L_p), and hence $J_{sc} \cdot L_p$ can be determined as the x -intercept or the inverse of the slope of a plot of $(\eta_q)^{-1}$ vs $[\alpha(\lambda)]^{-1}$, where η_q = quantum efficiency of electron-hole generation and $\alpha(\lambda)$ is the absorption coefficient. From Figure 2 it was thus found that L_p increased from 0.54 μm to 0.66 μm owing to Ru surface modification. A further contribution to the increase of J_{sc} is the increase of effective surface area on matte-etching. It is to be noted that both matte-etching and Ru treatment are essential for the reported improvement.

It has been shown by Jastrzebski *et al.*⁵ that in the presence of surface recombination the effective minority carrier-diffusion length L_{eff} is reduced from the bulk value L_0 by

$$L_{eff}^2 = L_0^2 \left(1 - \frac{s}{s+1} \right) \exp \left(-\frac{Z}{L_0} \right),$$

where s is the reduced surface recombination velocity SL_0/D (D is the diffusion coefficient and S the surface recombination velocity). Thus increase of L_{eff} results from decrease of surface recombination velocity. For n-GaAs Nelson *et al.*⁶ has shown that for unmodified surfaces $S = 5 \times 10^5 \text{ cm sec}^{-1}$. Assuming $L_0 = 1.0 \mu\text{m}$ ($\mu_p = 385 \text{ cm}^2 \text{V}^{-1} \text{ sec}^{-1}$, $\tau_p = 10^{-9} \text{ sec}$) and excitation at the

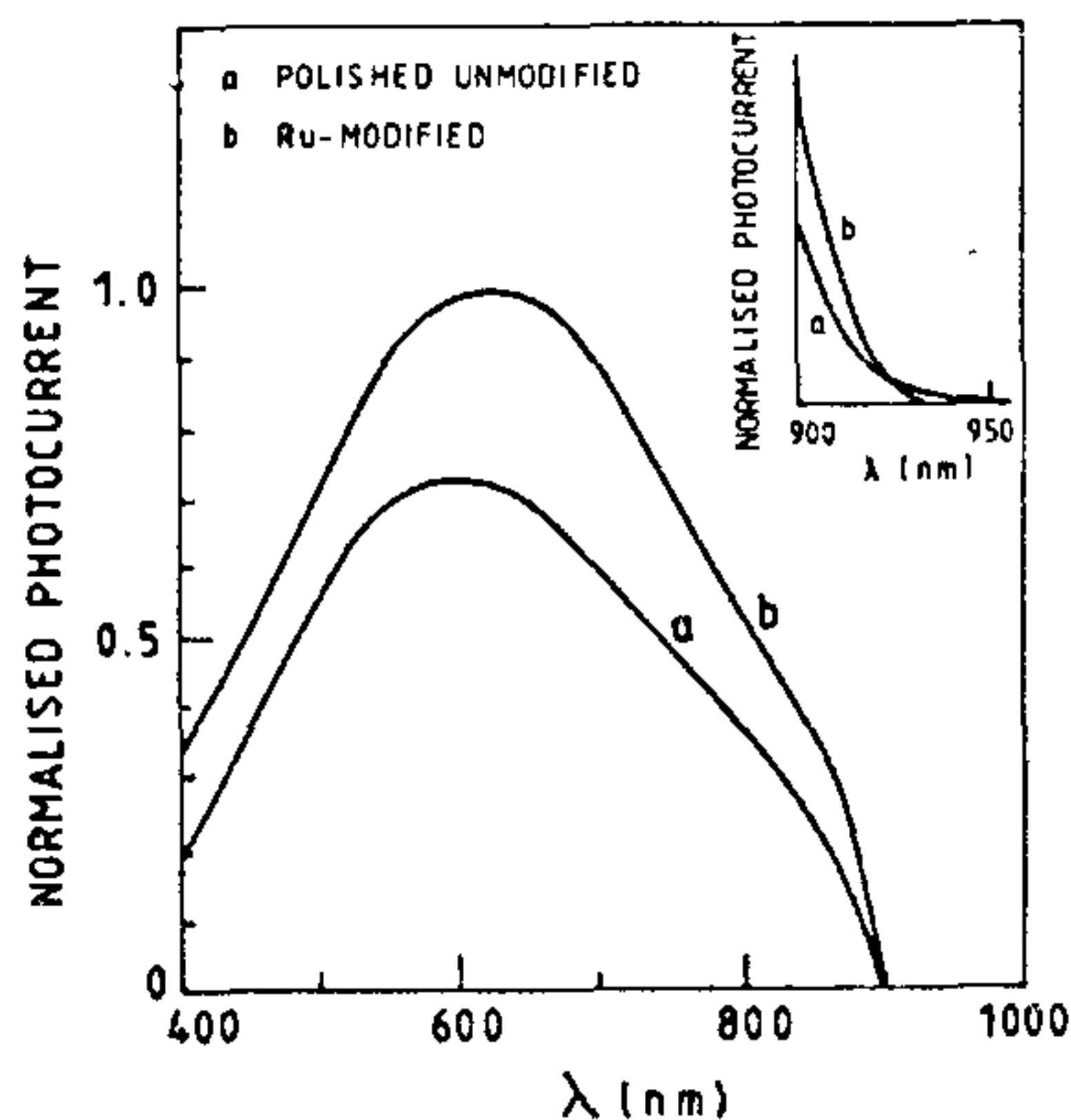


Figure 1. Spectral response of n-GaAs photoanode in 1 M KOH–0.1 M Na₂Te/Na₂Te_x–C redox-electrolyte system, showing increased photoresponse after Ru modification. Inset shows a reduction in sub-bandgap (900–950) nm response at a magnified scale.

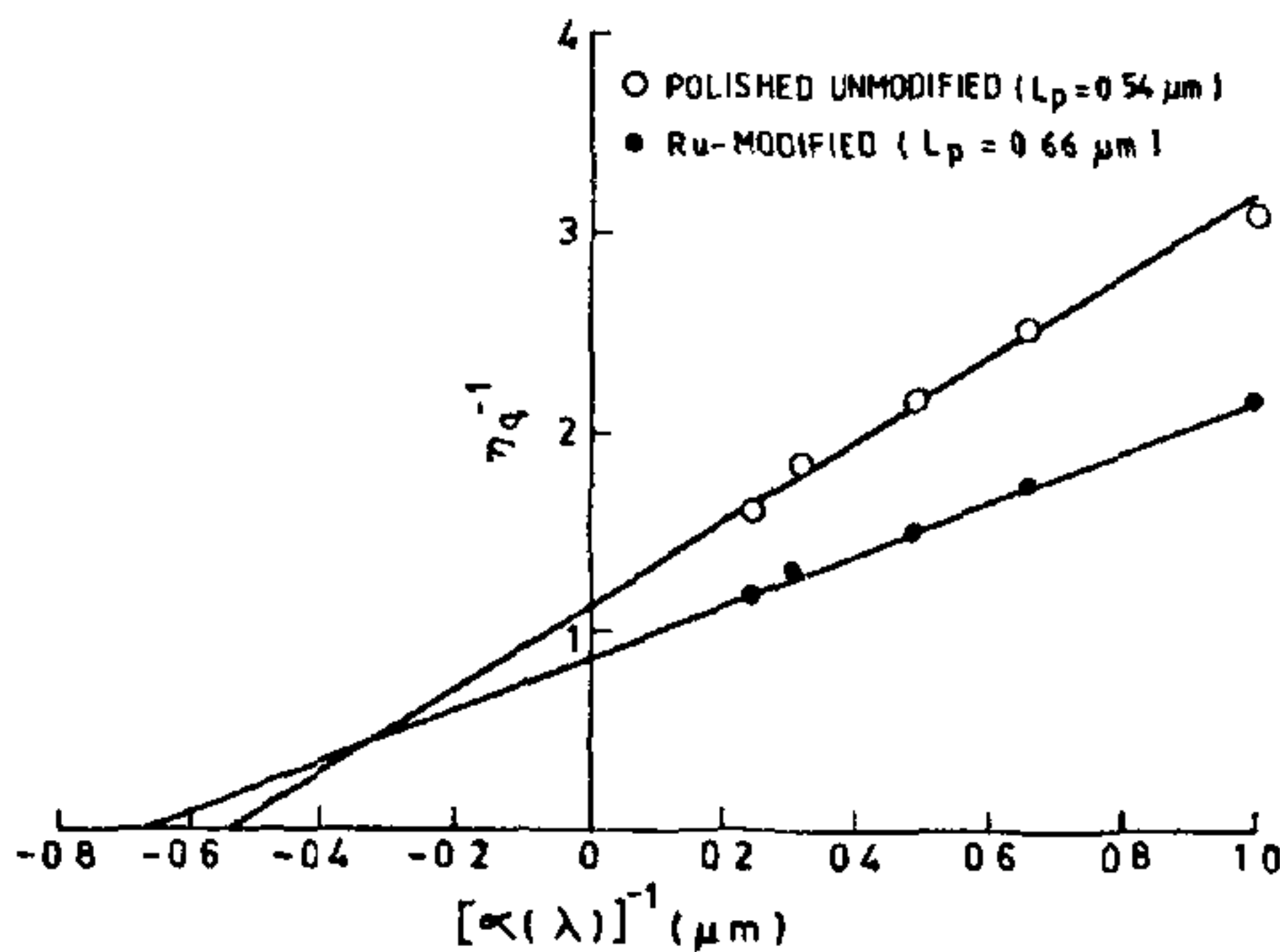


Figure 2. Plot of η_0^{-1} vs $\alpha(\lambda)^{-1}$ showing increased diffusion length (L_p) estimated from intercept. The $\alpha(\lambda)$ values were obtained from ref. 7 for $600 \text{ nm} \leq \lambda \leq 800 \text{ nm}$.

surface, i.e. $Z = 0$, it is found that increase in L_{eff} from $0.54 \mu\text{m}$ to $0.66 \mu\text{m}$ may be attributed to a reduction in S from $5.0 \times 10^5 \text{ cm sec}^{-1}$ to $2.65 \times 10^5 \text{ cm sec}^{-1}$.

The solar cell I - V characteristics were obtained using a 1.5 kW tungsten-halogen lamp whose intensity was calibrated using a standard silicon cell. Figure 3 shows the photo I - V curves [average of anodic (I_{sc} to V_{oc}) and cathodic (V_{oc} to I_{sc}) scan] of polished and Ru-modified samples. When polished GaAs (exposed area = $3 \text{ mm} \times 3 \text{ mm}$) was dipped in 1 M KOH 0.1 M $\text{Te}^{2-}/\text{Te}_x^{2-}$ it showed (Figure 3, curve a) a conversion efficiency (η) of 7.81% with $J_{\text{sc}} = 17.37 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.90 \text{ V}$, fill factor (FF) = 0.50 under AM1 condition. Exposure of the

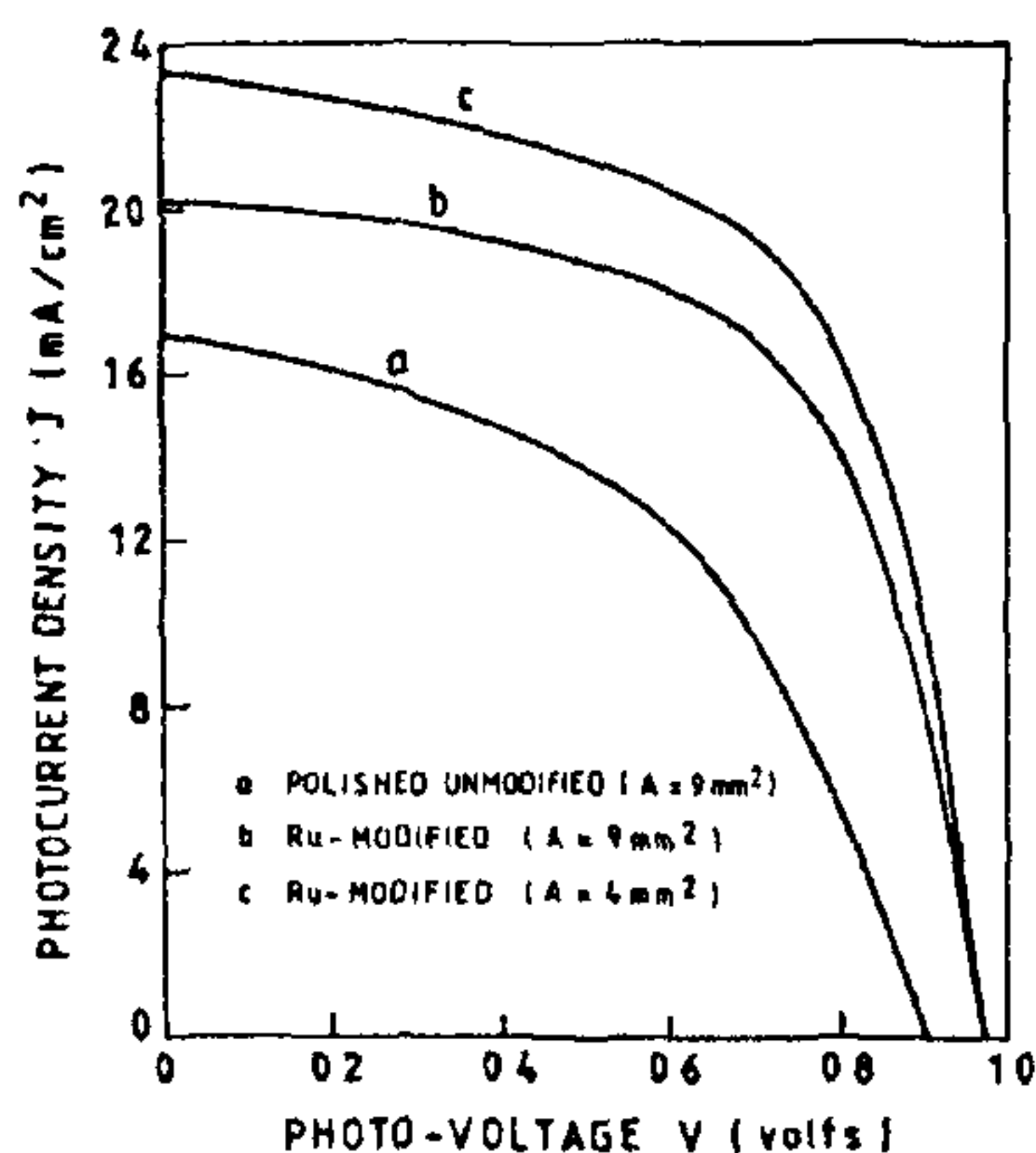


Figure 3. Photocurrent-voltage characteristics of n-GaAs photoanode in 1 M KOH 0.1 M Na_2Te , Na_2Te_x graphite redox-electrolyte system under AM1 condition a $\eta = 7.81\%$, b $\eta = 12.20\%$, c $\eta = 14.12\%$

etched GaAs to Ru^{3+} ions yielded (Figure 3, curve b) better I - V properties with $V_{\text{oc}} = 0.97 \text{ V}$, $J_{\text{sc}} = 20.30 \text{ mA cm}^{-2}$, FF = 0.62, $\eta = 12.2\%$. This V_{oc} value is the highest for GaAs PEC cells in an aqueous solution reported to date under AM1 condition. The improved FF from 0.50 to 0.62 may be attributed to reduced surface recombination at the photoanode as evident from lower ideality factor. It was also observed that photoanodes with smaller area ($2 \text{ mm} \times 2 \text{ mm}$) showed (Figure 3, curve c) higher efficiency, $\eta = 14.12\%$, with increased $J_{\text{sc}} = 23.49 \text{ mA cm}^{-2}$ owing to better charge transfer. The cells were found to be stable over 2-3 days.

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Highly saline fluid inclusions in Chamundi granite, South India

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Fluid inclusions in minerals and rock represent a potentially valuable source of information about the composition and density of fluids present during the formation and evolution of rocks. Our preliminary studies on Chamundi granite have indicated presence of highly saline inclusions (up to 50-60 wt.% NaCl equivalent) as well as low-salinity inclusions (8 to 22 wt.% NaCl equivalent). Data on temperature of homogenization suggest that they represent remnant fluids of magmatic origin trapped in minerals.

STUDIES on fluid inclusions in granitic rocks have shown the presence of H_2O -rich, aqueous and melt inclusions¹. Presence of CO_2 -rich inclusions and CO_2