

Search for cheap and efficient counter electrodes for some redox couples for potential aqueous PEC solar cells[†]

Jayati Datta & Kiron K Kundu*

Physical Chemistry Laboratories, Jadavpur University
Calcutta 700 032, India

Received 8 September 1993; revised and accepted 18 April 1994

Electrocatalytic activities of some noble metal [M = Pt, Pd, Rh, Ru and Au]-coated graphite, (C)M, platinized platinum (Pt)Pt, as well as bare Pt and C electrodes have been studied for the redox couples like hydroquinone-quinone (QH₂/Q) and ferrocene-ferricinium (Foc/Fic⁺) in water by determining the rate constant (*k_s*) of the redox reactions by cyclic voltammetric (CV) measurements. As on commonly used bright Pt, CVG's for Foc/Fic⁺ system on most of the metallized surfaces are characterized by single cathodic and anodic peaks and found to be quasi-reversible. Exactly similar behaviour is exhibited in the case of H₂Q/Q redox system in 1M H₂SO₄ solution. The observed order of *k_s* values based on apparent area of 1 cm² on different surfaces is found to be (C) Ru > Pt(Pt) > (C)Rh > Pt > (C)Pd > (C) > (C)Ir ≥ (C)Au > (C)Pt for QH₂/Q redox system (C(Au ≥ (Pt)Pt > (C)Pt ≈ (C)Pd ≈ (C)Ru > (C)Ir > Pt > C for Foc/Fic⁺ system. The observed orders are shown to be dictated by the roughness factor as well as the combined effect of 'electronic' and 'geometric' characters of the polycrystalline metallized surfaces guiding differently the coverage (θ) by solvent water molecules (θ_w) and the involved redox species (θ_r).

Search for cheap and efficient counter electrodes is as important as that of photoelectrodes for the development of practical photoelectrochemical (PEC) solar cells. But studies on that aspect are yet abysmally small^{1a-d}. As a part of comprehensive studies to that effect we have recently reported^{2a-f} the electrocatalytic activities of noble metal metallized graphite electrodes for some potential redox couples like I₂/I⁻, Br₂/Br⁻, Fe^{2+/3+}, Fe(CN)₆^{4-/3-} in water/nonaqueous media as obtained from cyclic voltammetry/polarization studies. As has been observed earlier for various other electrochemical reactions³⁻⁷, metallized graphite electrodes are found to be as efficient as pure noble metals like Pt, Pd etc, which are usually used

as indicating electrodes for various redox reactions because of their intrinsic electrocatalytic activities.

In the present note we report the electrode kinetic studies of redox processes like Q/H₂Q and Foc/Fic⁺ in water on bare Pt and graphite (C), platinized platinum (Pt)Pt and on some electrochemically deposited noble metal surfaces on carbon substrates (C)M with M = Pt, Pd, Rh, Ir, Ru and Au at 25°C using cyclic voltammetric technique. The cyclic voltammograms (CVG) were taken at varying sweep rates ranging from 2 to 400 mV s⁻¹ for each of the working electrodes with respect to a reference aqueous saturated calomel electrode [SCE(W)] at 25°. The rate constants (*k_s*) for the reactions were computed by means of appropriate fundamental equations formulated by Shain and Nicholson⁸ for quasi-reversible and irreversible systems, as observed in the present studies.

Experimental

The experimental set up and the entire procedure were exactly similar to that described in our earlier papers^{2(a-f)}. The working electrolytes used were quinhydron (the equivalent mixtures of Q and QH₂ (E. Merck, Germany) and ferricinium picrate (Fic⁺Pi⁻) prepared according to literature method. The starting material taken was anhydrous ferrocene (Sigma). SD (A.R. Grade) H₂SO₄ was used as the supporting electrolyte.

The solutions were made with triply distilled water and the formal concentrations of both hydroquinone and ferricinium (Fic⁺) salts were kept at 5 × 10⁻⁴ M in 1M H₂SO₄. Measurements were made by a set up consisting of Wenking Standard Potentiostat. [ST 72] coupled with a Wenking Voltage Scan generator [Model VSG72] and a Houston 2000 X-Y recorder.

Cyclic voltammograms were taken on the different electrode surfaces as mentioned earlier, with respect to SCE(W) at different scan rates ranging from 2-400 mV s⁻¹ applying the anodic potential range 0-900 mV for all the electrodes with QH₂/Q system and 0-600 mV for all the electrodes with Foc/Fic⁺ system. The essential CV parameters namely anodic peak potentials (*E_{p,a}*) and anodic peak currents (*i_{p,a}*) observed under different scan rates (ν) on different metallized surfaces for the QH₂/Q and (Foc/Fic⁺) systems are presented in Tables 1 and 2 respectively.

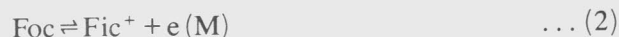
[†]Proc. 4th Asian Chem. Conf. Beijing, China, Aug. 1991. Proc. 6th Conf. on Electrochemical Power Sources, New Delhi, Dec. 1991.

Table 1—Cyclic voltammetric parameters E_p (mV) and i_p (mA/cm²) of redox reaction of Q/QH₂ system in water at 25°C on different electrodes

Scan rate mV s ⁻¹	Parameters	Electrodes								
		(Pt)Pt	Pt	C	(C)Pt	(C)Pd	(C)Ir	(C)Ru	(C)Rh	(C)Au
400	$-E_p$	574	631	794	588	621	532	483	711	588
	i_p	1.05	2.08	0.71	1.21	2.60	1.5	4.62	111.5	16.92
300	$-E_p$	—	—	—	—	602	527	—	—	579
	i_p	—	—	—	—	2.19	1.25	—	—	—
200	$-E_p$	555	607	771	565	—	518	469	687	541
	i_p	0.73	1.39	0.50	0.85	—	0.96	3.06	73.07	10.19
100	$-E_p$	541	602	748	555	574	508	460	664	518
	i_p	0.48	1.20	0.36	0.64	1.29	0.67	1.96	40.39	6.73
50	$-E_p$	532	593	738	541	551	494	450	654	508
	i_p	0.33	0.80	0.26	0.43	0.89	0.46	1.31	22.54	4.15
30	$-E_p$	527	—	724	537	532	—	447	640	499
	i_p	0.27	—	0.19	0.35	0.62	—	1.02	15.12	3.46
20	$-E_p$	527	588	720	532	518	489	447	—	494
	i_p	0.22	0.47	0.15	0.30	0.54	0.25	0.81	—	2.54
10	$-E_p$	522	588	710	518	494	485	447	616	485
	i_p	0.16	0.44	0.11	0.21	0.39	0.19	0.52	5.0	1.85
5	$-E_p$	517	588	701	508	494	480	—	616	480
	i_p	0.12	0.26	0.07	0.15	0.32	0.12	—	3.46	1.14
3	$-E_p$	508	—	—	494	—	—	—	—	—
	i_p	0.11	—	—	0.12	—	—	—	—	—
2	$-E_p$	508	—	701	—	494	471	—	616	471
	i_p	—	—	0.05	—	0.15	0.08	—	1.54	0.65
1	$-E_p$	508	—	—	480	494	471	—	—	471
	i_p	0.06	—	—	0.08	0.10	0.06	—	—	0.40

Results and discussion

Some typical voltammograms for QH₂/Q and Foc/Fic⁺ redox systems are shown in Figs (1) and (2) respectively. The cyclic voltammograms are characterised by single anodic and corresponding cathodic peaks for the electrochemical processes:



on all the electrode surfaces indicating similar mechanism being involved in all the cases. In the present case of QH₂/Q redox system since the redox reaction is studied at a low acidic pH (1M H₂SO₄) the whole system behaves as two overlapping single electron transfer reactions imparting the overall reaction as depicted in Eq. (1).

In most of the cases, quasi-reversible nature has been observed, barring a few cases where ΔE_p , i.e. the potential difference between anodic and cathodic peaks, being greater than 250 mV indicates irreversibility on these surfaces.

Equation (3) was used for evaluating the diffusion coefficient (D_{ox}) of the oxidising species using bare Pt as the working electrode

$$i_{p,a,rev} = 2.68 \times 10^5 n^{3/2} C_{\text{ox}} D_{\text{ox}}^{1/2} \nu^{1/2} \quad \dots (3)$$

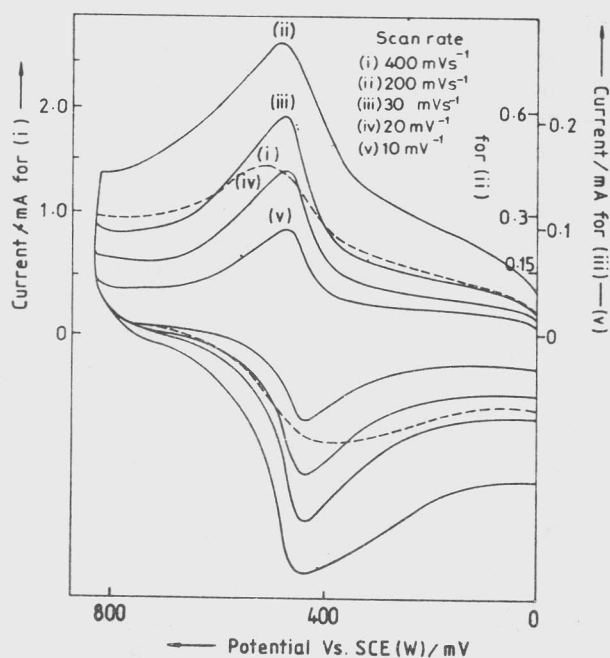
where n is the number of electrons involved in the overall reaction per mole of reactant, C_{ox} is the bulk concentration in mol cm⁻³ of the reactant oxidizing species, D_{ox} is diffusion coefficient of the oxidant in cm² sec⁻¹ and the scan rate ν is in Vs⁻¹. Since D_{ox} for a particular redox couple is essentially a bulk property, the values obtained using Pt as the working electrode were used for other electrode surfaces. The values of D_{ox} (vide Table 3) compare fairly well with the literature values⁹.

The values of the rate constant k_s of the redox reactions on most of the surfaces, where quasi-reversible behaviour were observed, were obtained by using Eq. 4

$$\log k_s = 0.52 - \frac{1}{2} \log(b/D_{\text{ox}}) + \frac{1}{2} \log \nu_c - 1.1 RT/bnF \quad \dots (4)$$

Table 2—Cyclic voltammometric parameters E_p (mV) and i_p (mA/cm²) of redox reaction of Foc/Fic⁺ system in water at 25°C on different electrodes

Scan rate mV s ⁻¹	Parameters	Electrodes							
		Pt	(Pt)Pt	C	(C)Pt	(C)Pd	(C)Ir	(C)Ru	(C)Au
400	$-E_p$	—	483	—	306	324	333	320	—
	i_p	—	5.32	—	1.63	1.21	2.89	5.31	—
300	$-E_p$	—	—	360	—	—	—	—	—
	i_p	—	—	1.25	—	—	—	—	—
200	$-E_p$	324	445	346	301	301	315	306	320
	i_p	0.55	4.26	0.83	1.06	1.0	1.85	3.46	2.89
100	$-E_p$	315	399	332	301	278	297	287	310
	i_p	0.50	3.24	0.68	0.96	0.71	0.96	2.19	1.85
50	$-E_p$	306	375	323	287	269	287	278	292
	i_p	0.49	2.04	0.55	0.87	0.47	0.77	1.25	1.58
30	$-E_p$	301	352	300	287	255	278	269	278
	i_p	0.39	0.77	0.35	0.53	0.34	0.49	0.90	1.04
20	$-E_p$	292	328	277	278	255	273	264	268
	i_p	0.36	0.46	0.24	0.35	0.27	0.39	0.68	0.92
10	$-E_p$	278	305	268	264	245	268	255	259
	i_p	0.32	0.46	0.16	0.19	0.17	0.26	0.51	0.65
5	$-E_p$	269	300	254	255	236	259	241	255
	i_p	0.23	0.31	0.11	0.14	0.12	0.19	0.26	0.51
3	$-E_p$	264	281	230	241	—	255	232	255
	i_p	0.17	0.14	0.07	0.06	—	0.15	0.20	0.42
2	$-E_p$	255	—	221	232	232	245	—	—
	i_p	0.10	—	0.04	—	—	0.12	—	—
1	$-E_p$	255	281	221	232	232	245	232	255
	i_p	—	—	—	0.05	0.69	0.10	0.10	0.30

Fig. 1—Cyclic Voltammograms on (C)Ru electrode at 25°C for QH₂/Q redox system

where Tafel slope $b = RT/\alpha F$, α being the transfer coefficient and the other terms have useful significance. The critical scan rates (ν_c) were obtained as usual^{1,8b} from the intersection of the observed linear plots of E_p versus $\log \nu$ at slow and high scan rate regions.

On the other hand, for these surfaces where the reactions were found irreversible, k_s values were obtained^{8b} using Eq. (5)

$$\log k_s = 0.52 - \frac{1}{2} \log(b/D_{ox}) - (I - E_{1/2})/b \quad \dots (5)$$

where I is the intercept of the observed linear plot of $(E_{p,a})_{irr}$ versus $\log \nu$ for each of the systems and $E_{1/2}$ values were obtained from Eq. (6)

$$E_{1/2} = E^\circ - (RT/nF) \ln \frac{f_{red}}{f_{ox}} \left(\frac{D_{ox}}{D_{red}} \right)^{1/2} \quad \dots (6)$$

The required E° values of the redox couple in water were obtained from literature¹⁰ and the contribution of activity coefficient factor f_{red}/f_{ox} by use of limiting form of Debye-Huckel equation¹¹.

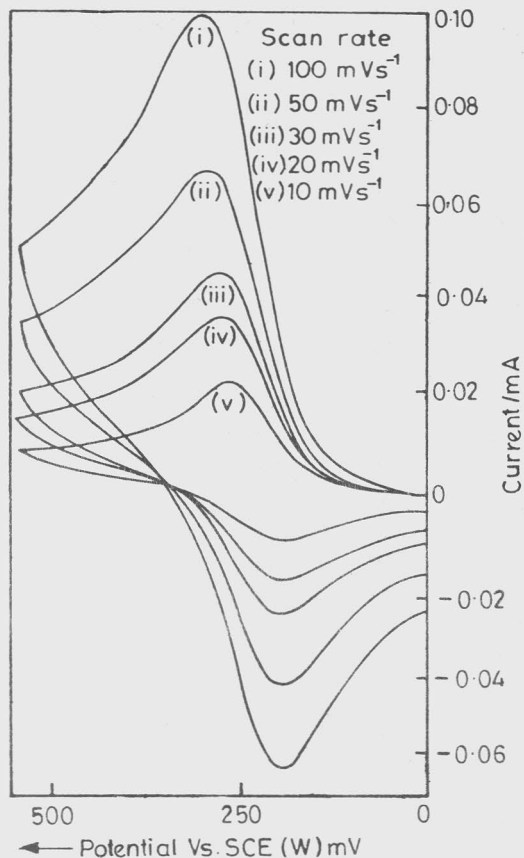


Fig. 2—Cyclic Voltammograms on (C)Pd electrode at 25°C for Foc/Fic⁺ redox system

D_{red} values were taken to be equal to those of D_{ox} for the corresponding redox couples since the D_{red} value of QH₂/Q couple obtained by using Eq. (3) and the observed cathodic peak currents ($i_{\text{p,c,rev}}$) in the reversible region of CV, as obtained from the auxiliary experiment with a solution containing $C_{\text{ox}} = C_{\text{red}} = 0.5 \times 10^{-3} M$ and $1.0 M H_2SO_4$, found to be equal to that of D_{ox} of the redox couple.

Table 4 presents the kinetic data ($k_{\text{s,app}}$) of anodic oxidation of QH₂/Q redox couple on a typical metallized surface viz (C)Ir obtained under different conditions of deposition. From this data it appears that the kinetic data on (C)Ir metallized surface are independent of the condition of deposition, but dependent on the amount of charge used for deposition. This is found to be true not only on (C)Ir surface but also on other (C)M surfaces and for both the redox couples. That is why attempts have been made to characterise the amount of deposition by keeping the time and current of deposition constant, namely 5 mA and 30 min, in all the cases.

Again, it would be evident from the data Table 4 that, diffusion coefficient values of the oxidant, D_{ox} for Foc/Fic⁺ system obtained on Pt are independent of the shape, size and nature of the substrates. So, D_{ox} values of the oxidants used for all the electrode surfaces were those obtained on bright Pt, as are given in Table 3. The k_{s} values so obtained being based on apparent area, may be denoted by $k_{\text{s,app}}$ and are listed in Table 3. A perusal of the data of $k_{\text{s,app}}$ on all the electrode surface reveals the following order: For QH₂/Q redox couple: (C)Ru > (Pt)Pt > (C)Rh > Pt > (C)Pd > (C) > (C)Ir \approx (C)Au > (C)Pt and for Foc/Fic⁺ redox couple: (C)Au \approx (Pt)Pt > (C)Pt \approx (C)Pd \approx (C)Ru > (C)Ir > Pt > C.

Similar orders for the other two redox couples namely Fe²⁺/Fe³⁺ (ref. 2b) and Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ (ref. 2c) systems reported earlier are as follows: For Fe²⁺/Fe³⁺ system Pt > (C)Ir > (C)Rh > (C)Ru > (C)Au \approx C > (C)Pt > (Pt)Pt \approx (C)Pd and for Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ system (C)Ru > (C)Au > C > (C)Ir \approx (C)Rh > (C)Pd > Pt > (C)Pt > (Pt)Pt.

Assuming that the observed order of $k_{\text{s,app}}$ values for any particular redox system serves as the measure of relative electrocatalytic activities of the electrode surfaces, the above order of $k_{\text{s,app}}$ values for the different redox systems indicates that the noble metal metallized surfaces over carbon substrates serve as more efficient electrocatalysts than the commonly used bare Pt or even platinumized Pt surfaces. Also, the relative order of the observed electrocatalytic activities are as expected, different for different redox couples.

The order of the $k_{\text{s,tr}}$ values obtained by dividing the observed $k_{\text{s,app}}$ values by the respective roughness factor (R_f)³ values of the metallized surfaces exhibit the following order: For QH₂/Q redox system: (C)Ru > (Pt)Pt > (C)Rh > (C)Au > (C)Ir > (C)Pd \approx (C)Pt. For Foc/Fic⁺ redox system: (C)Au > (C)Pd \approx (C)Ru > (Pt)Pt \approx (C)Ir > (C)Pt. For Fe²⁺/Fe³⁺ redox system: (C)Ir > (C)Ru \approx (C)Rh > (C)Au > (C)Pd > (C)Pt \approx (Pt)Pt and for Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ redox system: (C)Au > (C)Ru > (C)Ir > (C)Pd > (C)Rh \approx (C)Pt \approx (Pt)Pt.

Significantly, the observed relative orders of the $k_{\text{s,tr}}$ values on different noble metallized surfaces are also found to be quite different for different redox couples. Since the observed orders of $k_{\text{s,tr}}$ values hardly tally with the dictates of electronic factors¹¹⁻¹⁴ viz. work function and % d-band character of the noble metals involved, it appears that apart from electronic properties it is the geometric characters of the polycrystalline metallized surfaces with widely varying steps, kinks, edge vacan-

Table 3—Comparative views of $k_{s,app}$, $k_{s,tr}$ and $k_{s,tr}(C)M/k_{s,tr}(C)Pt$ on different noble metal-metallized surfaces for different redox couples

Electrode surface	Roughness factor (R_f)	QH_2/Q $D_{ox} = 3.5 \times 10^{-5} \text{ (cm}^2\text{s}^{-1}\text{)}$			Foc/Fic^+ $D_{ox} = 2.7 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$		
		$k_{s,app} \times 10^3$ (cm s^{-1})	$k_{s,tr} \times 10^5$ (cm s^{-1})	$k_{s,tr}(C)M$ $k_{s,tr}(C)Pt$	$k_{s,app} \times 10^2$ (cm s^{-1})	$k_{s,tr} \times 10^4$ (cm s^{-1})	$k_{s,tr}(C)M$ $k_{s,tr}(C)Pt$
Pt (bright)	—	5.5	—	—	0.7	—	—
(Pt) Pt	90	8.7	9.6	8.7	1.3	1.4	2.3
C (bare)	—	3.3	—	—	0.6	—	—
(C) Pt	185	2.0	1.1	1.0	1.1	0.6	1.0
(C) Pd	60	4.4	1.7	1.5	1.0	1.7	2.9
(C) Ir	70	2.4	3.4	3.1	0.8	1.1	1.8
(C) Rh	110	6.7	6.1	5.5	—	—	—
(C) Ru	60	10.6	17.7	16.1	1.0	1.7	2.9
(C) Au	50	2.3	4.5	4.1	1.4	2.8	4.6

Electrode surface	Roughness factor (R_f)	$Fe^{2+/3+}$ $D_{ox} = 1.2 \times 10^{-5} \text{ (cm}^2\text{s}^{-1}\text{)}$			$Fe(CN)_6^{4-/3-}$ $D_{ox} = 6.9 \times 10^{-6} \text{ (cm}^2\text{s}^{-1}\text{)}$		
		$k_{s,app} \times 10^3$ (cm s^{-1})	$k_{s,tr} \times 10^5$ (cm s^{-1})	$k_{s,tr}(C)M$ $k_{s,tr}(C)Pt$	$k_{s,app} \times 10^2$ (cm s^{-1})	$k_{s,tr} \times 10^4$ (cm s^{-1})	$k_{s,tr}(C)M$ $k_{s,tr}(C)Pt$
Pt (bright)	—	4.8	—	—	0.3	—	—
(Pt) Pt	90	0.1	0.1	4.0	0.04	0.04	1.0
C (bare)	—	0.4	—	—	2.2	—	—
(C) Pt	185	0.2	0.1	1.0	0.1	0.04	1.0
(C) Pd	60	0.1	0.3	2.7	1.0	1.6	40.0
(C) Ir	70	1.5	2.1	21.4	1.6	2.3	57.0
(C) Rh	110	1.3	1.2	12.0	1.2	1.1	28.0
(C) Ru	60	0.8	1.3	13.0	3.9	6.5	162.0
(C) Au	50	0.4	0.9	8.6	3.7	7.4	185.0

^aValues in this column are $k_{s,tr} \times 10^5$

Table 4—Effect of varying conditions of metallisation on $k_{s,app}$ for QH_2/Q system on (C)Ir electrode

Current (mA)	time (sec)	Q/C	$k_{s,app} \times 10^3$ (cm s^{-1})
0.65	1800	1.2	2.4
3.9	300	1.2	2.4
5.0	1800	9.0	8.0

Effect of shape and size of the metallized substrates on D_{ox} values for Foc/Fic^+ system

(Pt)Pt wire [$A = 0.1600 \text{ cm}^2$]; $D_{ox} = 2.2 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$

Pt foilim [$A = 0.66 \text{ cm}^2$]; $D_{ox} = 2.7 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$

(C)Pt rod [$A = 0.13 \text{ cm}^2$]; $D_{ox} = 3.1 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$

cies etc. that impart different coverages (θ) by solvent molecules (θ_w) and the redox reactants (θ_r) which play significant 'specific' roles in dictating the observed order of the desired electrocatalytic activities of the metallized surfaces.

Now, the electrocatalytic efficiencies of the metallized carbon, (C)M, relative to that of (C)Pt as denoted by $k_{s,tr}(C)M/k_{s,tr}(C)Pt$ for the reaction, are shown in Table 3. A perusal of these data indicates that a thin coating of noble metals on cheaper C substrates can serve as effective elec-

trocatalysts for these widely used redox couples. Furthermore, the widely used Pt or (Pt)Pt surfaces are not the most desired catalysts for these redox reactions. Also, contrary to the widely believed notion, the efficiency of the surfaces of other noble metals relative to that of the Pt could also be realized from the shift of anodic peak potential towards less anodic potentials on metallization than on platinization [vide Tables 1 and 2].

According to Ramraj and Natarajan⁵ the rate of $Fe^{2+/3+}$ reaction is increased remarkably by metallation of Ru as compared to other noble metals on conducting polymer coated Pt electrodes and this is consistent with the effectiveness of Ru observed in our study for $Fe^{2+/3+}$ redox couple.

Again, according to Bockris and coworkers¹⁴ some specifically adsorbed species may form a bridge between the electrode and reactant so as to facilitate the electron transfer reaction. Thus a comparative analysis of the results of $Fe(CN)_6^{4-/3-}$ system with those of $Fe^{2+/3+}$ system reveals that although a similar mechanism is involved, the π -bonding of CN^- ligands forming a conducting sheath around the iron nucleus facilitates electron tunnelling during charge transfer process, and hence the $k_{s,tr}$ values for $Fe(CN)_6^{4-/3-}$ oxidation

process are larger than those for the oxidation reaction of Fe^{2+} ions which are shielded by H_2O molecules of hydration.

From a perusal of the data in Table 3, it appears that Ru-deposited surface is the best electrocatalyst amongst the other noble metal metallized surfaces for QH_2/Q redox system, while Au deposited surface is the best electrocatalyst for Foc/Fic^+ redox system.

Former studies⁵ on kinetics of Q/QH_2 on different metals also suggest that Ru acts differently as compared to other metals. In the case of Ru, due to simultaneous oxide formation during hydrogen adsorption and desorption, the chemisorbed oxide layers are more suitable for oxidation of organic substances like QH_2 .

On the other hand, a study⁶ on the oxidation of ferrocene in ACN reveals that it is Au deposited surface which is found to be quite stable with largest rate constant values as compared to other metals, similar to what has been observed in the present study as well. Comparative data in Table 3, on the other hand, suggest that deposits of Ir and Ru are the most effective electrocatalyst for $\text{Fe}^{+2/+3}$ system and Au and Ru for $\text{Fe}(\text{CN})_6^{4-/-3-}$ system, and that k_s values for the latter system are larger than those for the former one.

However, these selective behaviour of the redox systems towards the metal surfaces are no doubt partially due to the intrinsic and specific property of the metals. And in our previous papers^{2b,c} where $\text{Fe}^{2+/-3+}$ and $\text{Fe}(\text{CN})_6^{4-/-3-}$ redox reactions have been reported, attempts have been made to correlate the kinetic results with the electronic work function and % *d*-band character of the metals, contrary to what has been observed by Bockris and coworkers¹⁴ for pure metals, the k_s values of coated surfaces are independent of these factors. Consequently, it was suggested that the order of k_s values on different noble metal metallized surfaces on graphite (C)M were largely dictated by geometric rather than electronic character of the deposits.

In fact, although the condition of electrochemical deposition being same for the different metal-coatings and with the basic assumption that a monolayer of metallation occurs in each case, it is quite likely that the geometric character of the polycrystalline deposits of different metals will vary to a large extent with widely varying kinks and edges of the growth, that would induce different values of coverages by solvent water dipoles (θ_w) and redox reactants (θ_r) for the different redox couples. Evidently, the amalgamated effects of both electronic and geometric properties of the

deposited surfaces are responsible for the observed order of electrocatalytic activities.

Thus, despite the fact that it is formidably difficult to assign the exact cause of the observed orders of relative electrocatalytic activities of the deposited surfaces of different noble metals on C substrates in particular, it may be concluded that these results help us to select the most effective electrocatalyst that would serve as the desired cheaper counter electrodes for these redox couples in water and possibly for other electrochemical solvents like ACN, DMF, PC etc. which are likely to be suitable for potential nonaqueous PEC solar cells^{15,16}. Thus it is evident that cost effective counter electrodes required for practical PEC solar cells can be achieved by replacing the costly Pt electrodes by cheaper C substrates with only a thin coating of noble metals without any loss of electrocatalytic efficiency. And the choice of metallized surfaces for the different redox systems in water should be Ir and Ru for $\text{Fe}^{+2/+3}$, Au and Ru for $\text{Fe}(\text{CN})_6^{4-/-3-}$, Ru for Q/QH_2 and Au for Foc/Fic^+ redox systems.

Acknowledgement

Thanks are due to UGC, New Delhi, and Govt. of India for providing a Research Associateship to J Datta.

References

- (a) Memming R, *Electrochim Acta*, 25 (1980) 77.
(b) Rajeshwar K, Singh P & Bow J Du, *Electrochim Acta*, 23 (1978) 1117.
(c) Heller A & Miller B, *Electrochim Acta*, 25 (1980) 29.
(d) Memming R, *Photochemical conversions, Storage of solar energy*, Proc 8th Int Conference, edited by P Ezio, S Marie & D Neth (1991) 193 and 393.
- (a) Datta J, Bhattacharya A & Kundu K K, *Bull chem Soc Japan*, 61 (1988) 1735.
(b) Datta J & Kundu K K, *Bull Electrochem*, 6(5) (1990) 542.
(c) *Bull Electrochem*, 7(1) (1991) 4.
(d) Datta J, Sinha S & Kundu K K, *Indian J Chem*, Press.
(e) Datta J & Kundu K K, *Bull Electrochem*, communicated.
(f) Bhattacharya S & Kundu K K, *Indian J Chem*, press.
- (a) Guha P K, Bhattacharya A & Kundu K K, *Indian J Chem*, 28A (1989) 267.
(b) Guha P K, *PhD Thesis*, Jadavpur University, India (1987) and the relevant references therein.
- (a) Ray S K, Talukdar H & Kundu K K, *Bull Electrochem*, 6(5) (1990) 559.
(b) S K Ray, Datta J & Kundu K K, (i) *Indian J Chem*, 31A (1990) 86; (ii) 32A (1993) 303.
- Ramraj R & Natarajan P, *Indian J Chem*, 28A (1989) 187.
- Biryol I, Kabasakalogu H & Uneri S, *Bull Electrochem*, 6(9) (1990) 793.
- Wipf D O & Wightman R M, *Anal Chem*, 62 (1990) 98.
- (a) Nicholson R S & Shain I, *Anal Chem*, 36 (1964) 706.
(b) Gileadi E, Kirowa-Eisner E & Penciner J, *Interfacial*

- electrochemistry-An experimental approach* (Addison-Wesley, Massachusetts) 1975.
- 9 *Handbook of Chemistry and Physics*, edited by R C Weast (The Chemical Rubber Co) 52nd Edition (1942).
 - 10 Glasstone S, *An introduction to electrochemistry* [D Van Nostrand Co Princeton, USA) (1972) p 293.
 - 11 Bockris J O'M & Reddy A K N, *Modern electrochemistry*, Vol 1 (Plenum Press, New York) 1970.
 - 12 (a) Biegler T, *Aust J Chem*, 26 (1973) 2587.
(b) Barna G G, Frank S N & Teharani T H, *J electrochem Soc*, 129 (1982) 746.
(c) Miaw C L, Rusling J F & Owlia A, *Anal Chem*, 62 (1970) 268.
 - 13 Mooto S & Furuya N, *J electroanal Chem*, 167 (1984) 309.
 - 14 Bockris J O'M, Mannan R J & Damjanovic A, *J chem Phys*, 48 (1968) 1898 and the relevant references therein.
 - 15 Ellis A B, Okaiser S W & Wrighton M S, *J electrochem Soc*, (1976) 6835.
 - 16 Talukdar H, Bhattacharya S & Kundu K K, *Indian J Chem*, communicated.