Short communication

The effect of the matrix on the electro-catalytic properties of methanol tolerant oxygen reduction catalysts based on ruthenium-chalcogenides

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Abstract

In this work, a catalyst based on nanostructured $Ru_xMo_ySe_z$ compounds was prepared by thermolysis of their carbonyl compounds in organic solvents. Evaluation of the catalytic activity was carried out via cyclic voltammetry on carbon paper. Synthesized catalyst was supported either by carbon black (Vulcan XC-72) or by polyaniline coated carbon black. The oxygen reduction activity and methanol tolerance of both electrodes was compared with commercial E-TEK 20% Pt–C electrode and polyaniline coated commercial E-TEK 20% Pt–C electrode. Characterisation of the catalysts was made using XRD and SEM. An important increase in the oxygen reduction reaction rate was observed using polyaniline coated carbon black matrix.
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1. Introduction

Direct methanol fuel cells using proton exchange membrane (PEMDMFC) are promising candidates for applications ranging from portable power sources (battery replacement applications) to power sources for future electric vehicles because of their safety, elimination of fuel processor system, thus, simple device fabrication and low cost.

However, there are also open questions related to DMFCs. One serious drawback is the methanol crossover from the anode to the cathode space of the membrane electrode assembly. This methanol crossover leads to an efficiency loss due to the formation of "mixed potentials" which result from methanol oxidation at the current state-of-the-art platinum cathode catalysts. One of the strategies may be considered to overcome this disadvantage the use of oxygen reduction catalysts, which are insensitive towards methanol.

The development of an alternative oxygen reduction electro-catalysts to platinum has been an important aim. This is also desirable as means of reducing costs. Recent advances have culminated in different kind of electro-catalysts, these include:

- Macrocyclic complexes, particularly those with N-based ligands such as porphyrins and phthalocyanins [1–4], and derivatives such as Fe-tetranitrophenyl-porphyrine (Fe-PP(NO$_2$)$_4$) [5] that have proved very active but do not show ideal stability behaviour.
- Transition metal oxides, especially those with structures allowing easy exchange of oxygen [6]. These have usually exploited the perovskite or pyrochlore structure. But these compounds are not stable in acid and even in alkaline solution.
- Transition metal sulfides based on Chevral phases characterised by a central octahedral metal cluster in which the delocalisation of electrons leads to high electron conductivity [7–11].
- Amorphous transition metal sulphide phases adsorbed on active carbons [10–13].
- Ruthenium molybdenum chalcogenides prepared by chemical synthesis from their carbonyl compounds [14–16].

The last method is based on the synthesis of materials under inert gas atmosphere (N$_2$) from their carbonyl compounds and chalcogens. The preparation of metal clusters by de-carboxylation of metal carbonyl clusters is effected by the removal of the –CO ligands. The reaction of carbonyl clusters with elemental chalcogenide generates a variety of polynuclear compounds with d-state coordination center [17,18]. It has been

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reported that polynuclear molecular clusters are small enough to be considered as quasi-molecular metal clusters rather than metallic particles. Their catalytic properties are distinct from those of metallic particles. Transition metal chalcogenide cluster compounds are of considerable interest owing to the coordination of oxygen to the transition metal complexes [19,20] and bimetallic interactions giving rise to catalytic processes [21–23].

In the present study we investigated the effect of the matrix on the $Mo_xSe_y–(CO)_n$ carbonyl cluster electro-catalyst prepared by a chemical synthesis [24,25] for molecular oxygen reduction reaction in acid medium. Carbon supported catalysts are applied to teflonized carbon paper substrates making an ink solution. The oxygen reduction is tested either directly on carbon paper catalyst as-prepared, or on modified carbon paper catalyst by polyaniline deposition.

2. Experimental

2.1. Preparation of catalyst

Carbon supported $Ru_xMo_ySe_z$ catalysts were prepared by the chemical reaction of the transition metal carbonyl compounds and Se with Vulcan XC-72R (Cabot Corporation) for 20 h at a temperature of 140 °C, under nitrogen in xylene solvent. The whole experiment was carried out under stirring and refluxing conditions [23–25]. The solution was filtered to recover the black solid, which was thoroughly washed with diethyl ether and dried in air at 90 °C over a night. Catalyst composition was 0.31 mg MoRuSe cm^{-2}, 18 w/o on Vulcan XC-72R.

Commercial E-TEK 20% Pt–C powders was used to compare the prepared chalcogenides catalysts.

2.2. Electrode preparation

The electrodes were prepared by applying either the catalyzed E-TEK or Ru chalcogenides carbon to teflonized carbon paper substrates (Toray) using Nafion and polyvinyl pyroolidone (PVP) (10:10 w/o dry electrode) as binder. In each case, approximately 8 mg catalyzed carbon, 200 µl Millipore water, corresponding Nafion and PVP were homogenized ultrasonically for 15 min and then applied to the substrate with a spatula. The electrodes were then allowed to dry.

Dried electrodes were then modified by polyaniline (PANI) films. PANI films were formed on electrodes by cycling the potential continuously between −0.2 and 0.8 V (SCE) in a solution containing 0.5 M H_2SO_4 and 0.1 M aniline.

2.3. Electrochemical set-up

All experiments were performed in a classical three electrode cell with a Pt cage as counter electrode and a saturated calomel electrode (SCE) as reference. All the potentials are reported on the SCE scale. The working electrode was a teflonized carbon paper (Toray) (geometric area: 1 cm^2).

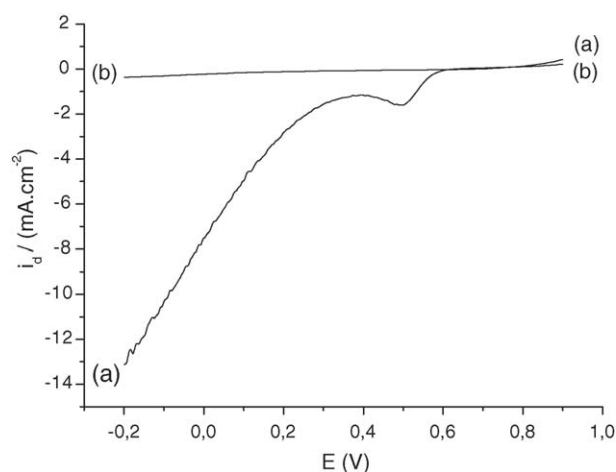Electrochemical experiments were performed using a Voltalab Impedance Spectroscopy.

Fig. 1. Polarisation curves for the oxygen reduction at 25 °C, 0.1 M HClO$_4$, 5 mV s^{-1} on: (a) polyaniline coated Vulcan XC-72 supported $Mo_xRu_ySe_z$ electrode and (b) Vulcan XC-72 supported $Mo_xRu_ySe_z$ electrode.

Electrolytic solutions were prepared from ultra pure water (Millipore) and Merck reagents (pro analyst for aniline, extra pure for HClO$_4$ and reagent grade for methanol). Aniline was purified further by distillation under vacuum (15 Torr) and other reagents were used as received.

3. Results

The electro-catalytic activity of the supported ruthenium based catalysts was tested in oxygen saturated 0.5 M H_2SO_4 as a function of temperature. Typical polarisation curves are given in Fig. 1. By comparing both of the curves, the matrix effect may be observed very clearly. By shifting the electrode potential to less positive values, an increasing reduction current can be observed. The polyaniline coated electrode shows a higher activity (about six times more) and reduction rate increase at more positive potentials (0.6 V in place of 0.1 V).

The effect of temperature on the reduction of oxygen both on carbon supported $Ru_xMo_ySe_z$ and PANI modified catalysts is studied in the range of 25–90 °C. Activation energy values are calculated from the slopes of the current densities versus $1/T$ plots (Figs. 2 and 3). Activation energy values are found
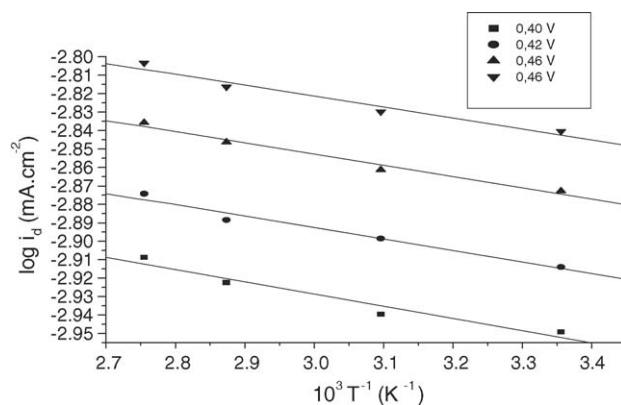

Fig. 2. Temperature effect on the reduction of oxygen on PANI coated carbon supported $Ru_xMo_ySe_z$ catalyst in 0.1 M HClO$_4$, 5 mV s^{-1}.
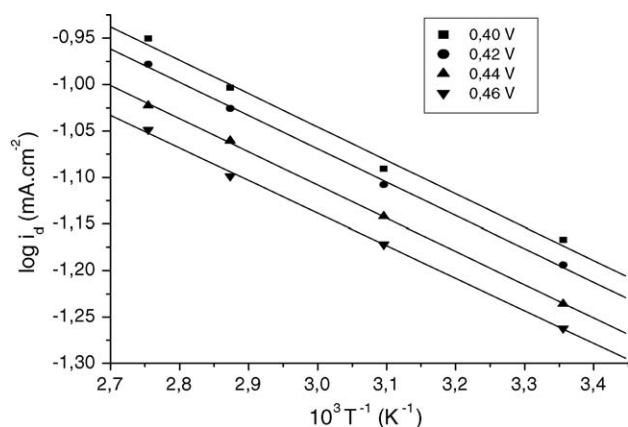
Fig. 3. Temperature effect on the reduction of oxygen on carbon supported $Ru_xMo_ySe_z$ electrode in 0.1 M HClO$_4$ at 5 mV s^{-1} scan rate.

Table 1
ΔH^* values of Vulcan XC-72 supported $Ru_xMo_ySe_z$ vs. potential

	E (V)			
	0.40	0.42	0.44	0.46
$\delta \log i/\delta(T^{-1})$	−0.35953	−0.35871	−0.35744	−0.35046
ΔH^* (kJ mol^{-1})	6.88397	6.86827	6.84395	6.71030

Table 2
ΔH^* values of PANI coated Vulcan XC-72 supported $Ru_xMo_ySe_z$ vs. potential

	E (V)			
	0.40	0.42	0.44	0.46
$\delta \log i/\delta(T^{-1})$	−0.0662	−0.06229	−0.06104	−0.05954
ΔH^* (kJ mol^{-1})	1.26754	1.19267	1.16874	1.1400

as 6.82662 kJ mol^{-1} (Table 1) for carbon supported $Ru_xMo_ySe_z$ and 1.19223 kJ mol^{-1} (Table 2) for PANI modified catalysts. It can be deduced that oxygen reduction on PANI modified catalysts is more feasible.

The effect of varying the sweep rate of voltage sweep at constant potential limits is examined and shown in Fig. 4. The current densities vary linearly with increasing scan rate (mV s^{-1}), a linear relationship between peak current and square root of scan rate is apparent for an irreversible diffusion controlled process for both of the catalysts.

The Tafel plot analysis of the reduction peak was also realised for carbon supported $Ru_xMo_ySe_z$, PANI modified catalysts under the same conditions (Fig. 5). The αn values calculated from the slopes of the straight lines are given in Table 3.
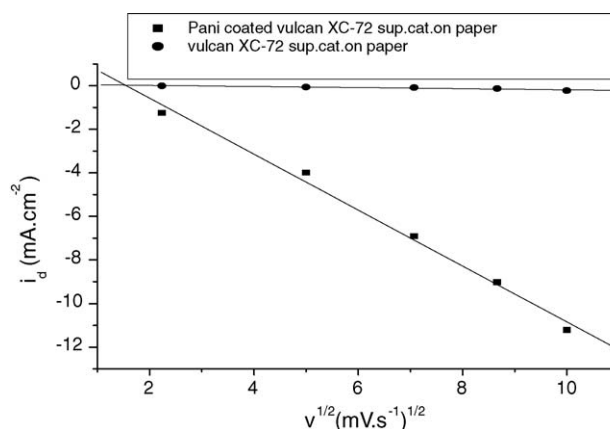

Fig. 4. Peak current dependence vs. square root of scan rate at polyaniline coated Vulcan XC-72 supported catalyst and Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst at 25 °C, 5 mV s^{-1} in 0.1 M HClO$_4$.
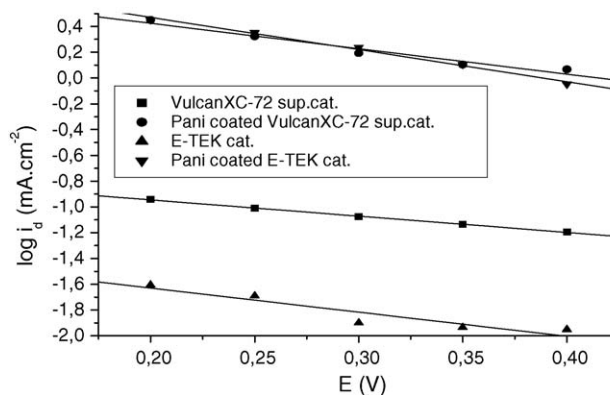

Fig. 5. Tafel plots for the oxygen reduction of polyaniline coated Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst and Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst at 25 °C, 5 mV s^{-1} in 0.1 M HClO$_4$.

A well-known drawback of platinum for the oxygen reduction reaction is its tendency to become poisoned in the presence of methanol [23]. This is a critical problem in methanol fuel cells. For this reason, the effect of the presence of methanol during oxygen reduction is investigated for both on carbon supported $Ru_xMo_ySe_z$ and PANI modified catalysts in oxygen saturated 0.5 M H$_2$SO$_4$ + 1 M CH$_3$OH solution. Fig. 6 shows the oxygen reduction on carbon supported catalyst in the absence and in the presence of methanol. Fig. 7 shows the oxygen reduction on PANI modified catalyst in the absence and in the presence of methanol. Fig. 8 shows the comparison of methanol dependence of PANI coated Vulcan XC-72 supported catalysts and Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalysts. A significant reduction
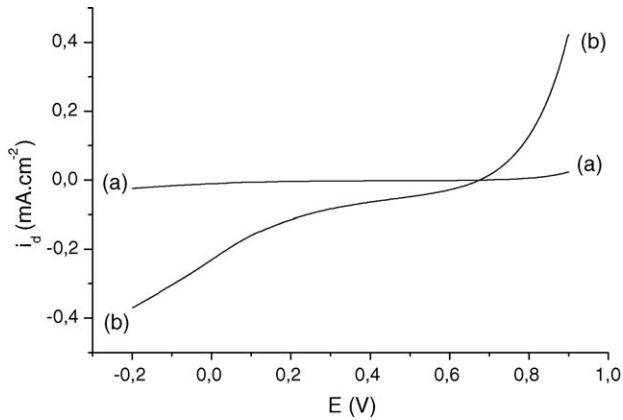
Table 3
Comparison of n transferred electron numbers of Vulcan XC-72 supported $Ru_xMo_ySe_z$, PANI coated Vulcan XC-72 supported $Ru_xMo_ySe_z$, E-TEK catalyst and PANI coated E-TEK catalyst

	$\delta \log i/\delta E$	αn	n
Vulcan XC-72 supported $Mo_xRu_ySe_z$	−1.26316	0.074695	0.14939
PANI coated Vulcan XC-72 supported $Mo_xRu_ySe_z$	−1.97484	0.11678	0.23356
E-TEK catalyst	−2.20951	0.129342	0.258684
PANI coated E-TEK catalyst	−2.49536	0.146075	0.292151

Fig. 6. Polarisation curves of oxygen reduction on Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst at 25 °C, 5 mV s^{-1}: (a) in the presence of 1 M CH$_3$OH and (b) in the absence of methanol.
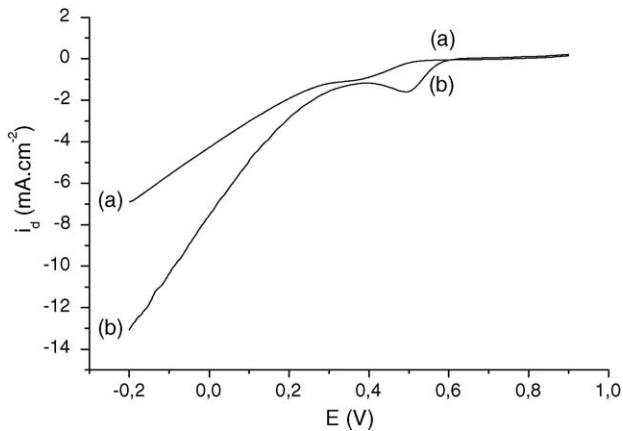

Fig. 7. Polarisation curves of oxygen reduction at 25 °C, 5 mV s^{-1}, on polyaniline coated Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst: (a) in the presence of methanol (0.1 M HClO$_4$ + 1 M CH$_3$OH) and (b) in the absence of methanol (0.1 M HClO$_4$).
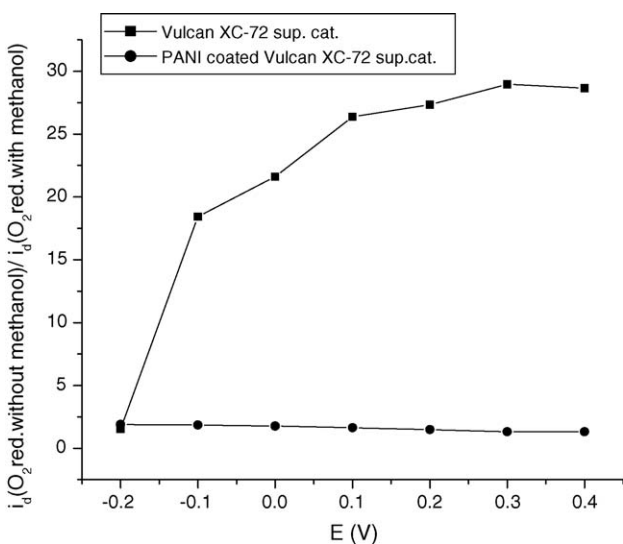

Fig. 8. Comparison of methanol dependence of PANI coated Vulcan XC-72 supported catalysts and Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalysts.
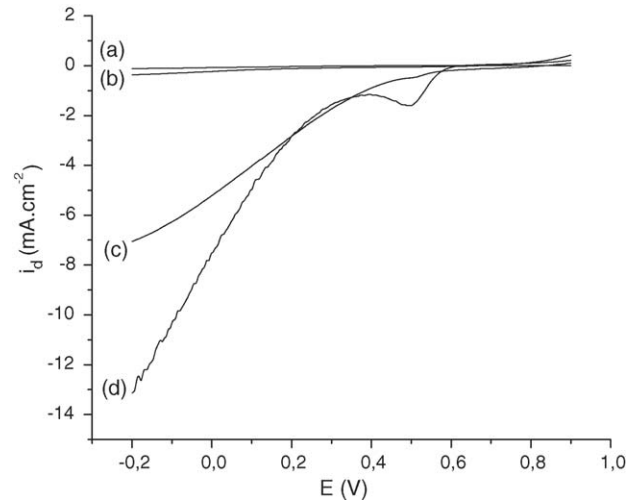

Fig. 9. Comparison of the oxygen reduction reaction at 25 °C, 0.1 M HClO$_4$, 5 mV s^{-1}: (a) E-TEK 20% Pt/C catalyst, (b) Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst, (c) PANI modified E-TEK 20% Pt/C catalyst and (d) PANI modified Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst.

current density is obtained in the case of PANI modified electrode.

The results observed by the electrodes prepared using Ru chalcogenide catalysts are compared with E-TEK 20% Pt/C commercial powder loaded electrodes under the identical experimental conditions. PANI modified and non-modified electrodes are studied in the presence and absence of methanol (Figs. 9 and 10) and number of electrons transferred are calculated (Tables 3 and 4) from Tafel curves (Figs. 5 and 12). If we assume $\alpha = 0.5$, the number of electron transferred increase in the case of PANI modification both for Ru chalcogenide based catalysts and commercial E-TEK powder based catalysts. Ru chalcogenide based electrodes are found to be more
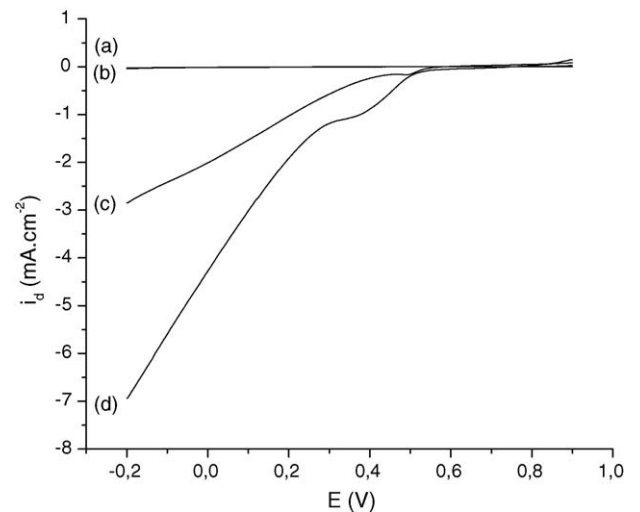

Fig. 10. Comparison of the oxygen reduction reaction at 25 °C, 5 mV s^{-1} in 0.1 M HClO$_4$ + 1 M CH$_3$OH: (a) Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst, (b) E-TEK 20% Pt/C catalyst, (c) PANI modified E-TEK catalyst and (d) PANI modified Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst.

Table 4
Comparison of n transferred electron numbers of Vulcan XC-72 supported $Ru_xMo_ySe_z$, PANI coated Vulcan XC-72 supported $Ru_xMo_ySe_z$, E-TEK catalyst and PANI coated E-TEK catalyst in the presence of methanol

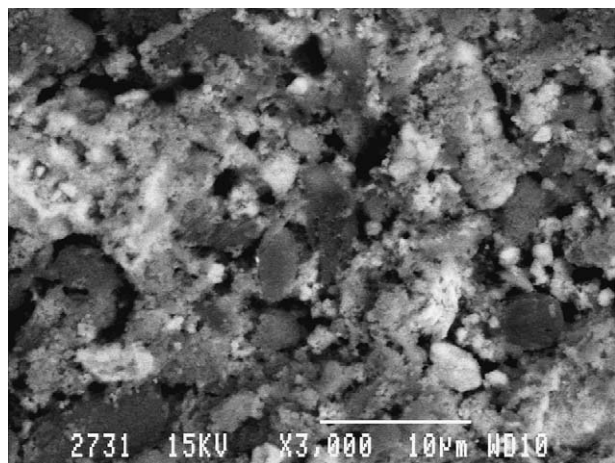|	$\delta \log i/\delta E$	αn	n
Vulcan XC-72 supported $Mo_xRu_ySe_z$	−1.3808	0.08165	0.16330
PANI coated Vulcan XC-72 supported $Mo_xRu_ySe_z$	−1.6166	0.09559	0.19119
E-TEK catalyst	−1.72889	0.101207	0.202414
PANI coated E-TEK catalyst	−3.14652	0.184193	0.368387

Fig. 11. SEM photograph of Vulcan XC-72 supported catalyst.

selective for the oxygen reduction in the presence of methanol (Fig. 12) (Table 4). Significantly increased oxygen reduction current intensity was observed using Ru chalcogenides based and PANI modified electrodes. SEM photograph of Vulcan XC-72 supported catalyst is given in Fig. 11. Nanosized catalyst particles or clusters are observed on the carbon supports.

The future works will going on the determination of partical sizes and the measurements of the performance of the Ru based electrodes under continuous flow conditions.
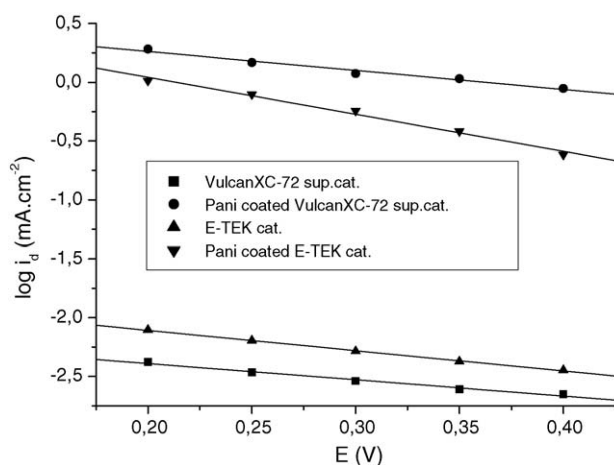

Fig. 12. Tafel plots of Vulcan XC-72 supported catalyst, E-TEK 20% Pt/C catalyst, PANI modified E-TEK catalyst and PANI modified Vulcan XC-72 supported $Mo_xRu_ySe_z$ catalyst at 25 °C, 5 mV s^{-1} and in 0.1 M HClO$_4$ + 1 M CH$_3$OH.

4. Conclusion

The present study shows that PANI modified $Ru_xMo_ySe_z$ catalysts have a good performance for oxygen reduction reaction even in the presence of methanol. The oxygen reduction reaction seems to occur under mixed control, the overall rate being determined by diffusion in solution and charge transfer kinetics. In the presence of methanol, the activity of PANI modified electrode was better than that of non-modified carbon supported, providing that PANI modification decrease the poisoning of the surface and increase probably the matrix conductivity. To provide comparative data, electrodes prepared under the identical experimental conditions from E-TEK 20% Pt/C powder was studied for the reduction of oxygen in the presence and absence of methanol either by PANI modification or without modification. According to the results the activity of the PANI modified Ru chalcogenide catalysts was found to be best than that of PANI modified E-TEK catalyst loaded electrodes even in the methanol presence. The number of electron transferred in the presence of methanol was higher using PANI modified E-TEK electrodes. This shows the selectivity of Ru chalcogenide electrodes toward oxygen reduction.

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