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Electrocatalytic properties of mixed transition metal tellurides (Chevrel-phases) for oxygen reduction

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Pseudobinary molybdenum cluster tellurides (Chevrel phases) with mixed transition metal clusters of the type $M_xMo_{6-x}Te_8$ (M = Pt, Os, Ru, Rh) and the binary phase Mo_6Te_8 have been synthesized, structurally characterized and electrochemically investigated with respect to their electrocatalytic properties for oxygen reduction. A correlation of the number of electrons per cluster unit (NEC) with the open circuit potential (o.c.p.) in saturated oxygen electrolyte was found. The limitation of the o.c.p. values are due to the mixed potential developed with each electrode material due to molybdenum oxidation. The lowest corrosion tendency and highest catalytic activity are found in the telluride phases when NEC (in the valence band) approaches 24.

1. Introduction

In recent years, Chevrel phases have been intensively studied with respect to their catalytic properties for oxygen reduction [1]. These cluster compounds can be classified in binaries (Mo_6X_8, X = S, Se, Te), ternaries ($M_xMo_6X_8$, M = intercalated metal guest ion) and pseudobinaries ($Mo_{6-x}M_xX_8$) in which molybdenum is partially substituted by another transition metal. The crystal structure (here, e.g., Mo_6Te_8) can be described as octahedral molybdenum clusters being surrounded nearly cubically by eight tellurium atoms as indicated in Fig. 1.

The number of electrons per cluster units (NEC) and thus the electronic parameters of the material can be varied by either intercalating guest cations into vacant lattice sites (Δ in Fig. 1) [2] or by substituting molybdenum partially through other transition metals with a higher number of valence electrons (e.g., Ru) [3]. In both cases, the variation of electrons delocalized in the cluster influences the filling of binding valence band states leading to significant changes in the crystal structure of the compound [4]. Thus, the physical and electrochemical properties (e.g., the electrocatalytic activity) of the material can be easily controlled by the NEC.

Several ternary phases of the type $M_xMo_6S_8$ (M = intercalated metal guest cation) have already been investigated in terms of their electrocatalytic properties for oxygen reduction [5]. However, these intercalation compounds have been found to be electrochemically unstable due to deintercalation processes at positive potentials. The highest activities have been reported for a few existing pseudobinary Chevrel phases $Mo_{6-x}M_xSe_8$ (M = Ru and Re, X = S, Se). In particular, $Mo_4Ru_2Se_8$ was found to be a very efficient oxygen reduction catalyst in acid medium with selective properties in the presence of methanol [5, 6]. The compound reduces O_2 to H_2O in a four-electron process with less than 4% of H_2O_2 formation [7]. Therefore, this material class is of general interest as potential cathode in methanol-air fuel cells. In this contribution we report on the synthesis, structural characterisation and electrocatalytic properties of several mixed cluster tellurides with respect to oxygen reduction in acid medium.

2. Experimental details

Pseudobinary Chevrel-Phases of the type $Mo_{6-x}M_xTe_8$ (M = Pt, Os, Ru and Rh) and Mo_6Te_8 have been synthesized by heating stoichiometric amounts of the elements (transition metals: Johnson Matthey, purity >99.99% and tellurium: Alfa/Ventron, m5N8) in sealed quartz ampoules for 24 h at 750 °C and thereafter for another 48 h at 1230 °C. After cooling the loose powders were agitated in the ampoule. To achieve homogeneous products the powders were again thermally treated at 1230 °C for 120 h. Phase analysis and determination of lattice parameters were performed with a powder diffractometer (Siemens D 500, working in a Θ/2Θ mode) using CuK_α radiation. However, most attempts to substitute molybdenum partially in the cluster gave multiphase mixtures, strongly dominated by metal ditellurides. Only Mo_6Te_8, $Mo_{5.8}Pt_{0.2}Te_8$, $Mo_{5.4}Os_{0.6}Te_8$, $Mo_5Rh_1Te_8$ and $Mo_4Ru_2Te_8$ could be obtained as one phase products. They were structurally characterised by powder X-ray diffraction and further investigated electrochemically. The hexagonal lattice parameters of the compounds and the calculated NEC are listed in Table 1. In order to confirm the validity of the X-ray structural characterization of these phases,

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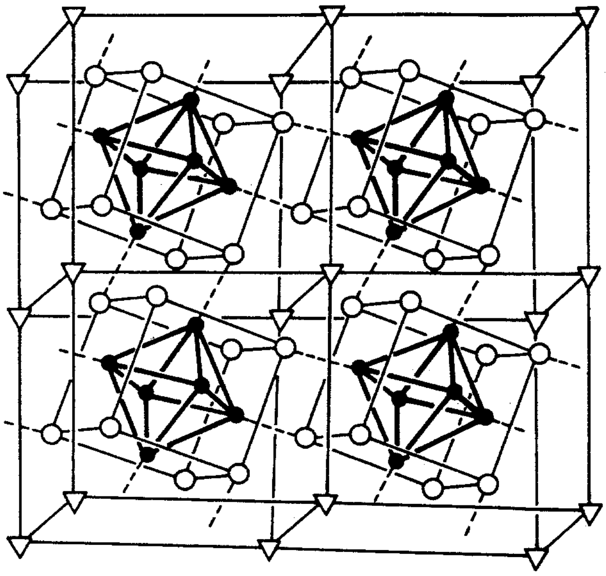

Fig. 1. Crystal structure of the binary Chevrel phase Mo_6Te_8 ((●) Mo, (○) Te); (△): site of metal atoms (e.g., Pb) in ternary compounds. In the case of pseudobinary phases (e.g., $Mo_4Ru_2Te_8$), molybdenum is partially substituted by a further transition metal (statistical distribution on regular Mo-cluster sites).

high resolution transmission electron microscopy (HRTEM), Philips CM12, was performed on the $Mo_{5.8}Pt_{0.2}Te_8$ phase to rule out the possibility of electrocatalysis induced by platinum particles. The powder was finely grounded in an agate mortar with a small amount of ethanol. A drop of ethanol containing the finely ground powder was placed on TEM grids (400 mesh copper with 5 nm amorphous carbon).

Electrodes were prepared by mixing the sieved powder (grain size: 20–40 µm) with 50 wt % carbon paste matrix (graphite powder (Aldrich) and paraffin oil (Merck p.a.)), pressing the mixture in Vespel (Polymid type SP-1, Dupont) holders, as described elsewhere [5]. All electrochemical measurements were carried out in a standard one compartment three-electrode electrochemical cell. Counter and reference electrodes were platinum and saturated calomel (SCE), respectively. The electrolyte was 0.5 M sulphuric acid, pH 0.3 (Merck, p.a.). Rotating disc electrode (RDE) experiments and determination of differential (double layer) capacity were carried out with a bipotentiostat, Model PM 3 and a rotating electrode (both from Pine Instruments), which were connected to a computer system (Apple Macintosh LC). Cyclovoltammetric experiments were performed with a PAR potentiostat Model 273 with automatic data acquisition software System 270 (EG&G). All experiments were performed at room temperature. Prior to measurement with oxygen the electrolyte was purged with nitrogen. Unless otherwise stated, all potentials are quoted with respect to the normal hydrogen electrode (NHE).

Table 1. Hexagonal lattice parameters of molybdenum cluster tellurides (Chevrel phases) with calculated number of electrons per cluster unit (NEC)

Compound	*NEC*	a_h/nm	c_h/nm	V_h/nm^3
$Mo_4Ru_2Te_8$	24	1.029 0(1)	1.137 6(2)	1.043 1(1)
$Mo_5Rh_1Te_8$	23	1.025 0(1)	1.152 0(2)	1.048 2(1)
$Mo_{5.4}Os_{0.6}Te_8$	21.2	1.022 9(2)	1.162 1(2)	1.053 2(1)
$Mo_{5.8}Pt_{0.2}Te_8$	20.8	1.022 3(1)	1.166 5(1)	1.055 7(1)
Mo_6Te_8	20	1.021 3(1)	1.167 6(2)	1.054 6(1)

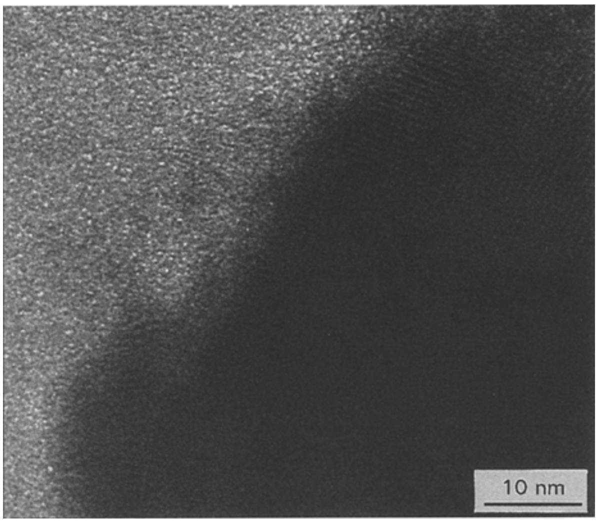

Fig. 2. Electron micrograph of $Mo_{5.8}Pt_{0.2}Te_8$.

3. Results and discussion

A typical transmission electron micrograph of $Mo_{5.8}Pt_{0.2}Se_8$ is shown in Fig. 2. The power spectrum analysis of this picture indicates lattice planes of 0.706 nm and 0.31 nm. These values agree very well with the calculated lattice constant of this phase for 101 (0.705 nm) and 113 (0.309 nm) *hkl* indices. Furthermore, a semiquantitative EDX analysis on different domains (analysed surface: ~0.16 µm^2) revealed a Mo : Te and Pt : Te ratio of 0.6 and 0.04 in comparison to the calculated 0.72 and 0.025, respectively. We conclude that the compound is a single phase, within experimental error (~15%), in agreement with the results obtained by X-ray diffraction.

To estimate the electroactive surface, S_a, of carbon paste supported electrodes, the charging current,

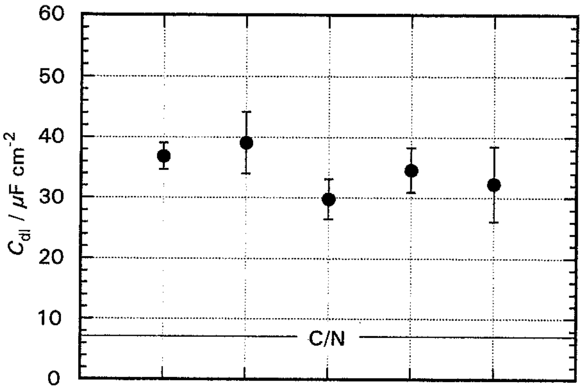

Fig. 3. Mean differential capacities (C_{dl}) of different $Mo_4Ru_2Te_8$, $Mo_5Rh_1Te_8$, $Mo_{5.4}Os_{0.6}Te_8$, $Mo_{5.8}Pt_{0.2}Te_8$, Mo_6Te_8 powders supported on carbon paste electrodes. A pure carbon paste electrode (C/N) is also shown for comparison.

($I_c = C_{dl}\,dV/dt$), of the double layer, ($C_{dl} \propto S_a$), was measured at 5, 10, 20, 35 and 50 mV s^{-1} in a potential range between 300 and 400 mV. Thereafter, the capacity (C_{dl}) was normalised to the geometrical electrode surface (0.19 cm^2). As shown in Fig. 3 the differential capacities among all samples investigated varied only in a small range. The sieve of the powders led to much more reproducible results as compared to Chevrel-phase nonsieved powder electrodes prepared in the same way [8]. Therefore, reproducible electrocatalytic current densities were obtained within a sample batch. Due to the fact that the capacities only varied between 30 and 45 μF cm^{-2} all samples could be directly compared to each other without further normalisation.

Table 2. Electronic and Tafel-parameters of oxygen reduction at different Chevrel phases in O_2-saturated 0.5 M H_2SO_4 (NEC = number of electrons per cluster)

Compound	*NEC*	U_{ocp}/mV	η^*/mV	log (i_0)	b/mV dec^{-1}
$Mo_4Ru_2Te_8$	24	720	510	−6.53	−112.7
$Mo_5Rh_1Te_8$	23	690	470	−6.00	−117.4
$Mo_{5.4}Os_{0.6}Te_8$	21.2	650	620	−5.98	−155.5
$Mo_{5.8}Pt_{0.2}Te_8$	20.8	620	580	−6.85	−119.3
Mo_6Te_8	20	590	650	−4.12	−305.1

* Overvoltage η determined at $i = 10^{-5}$ A cm^{-2} referring to E_0 (O_2/H_2O = 1.21 V at pH 0.3); i_0 in mA cm^{-2}, partly determined from extrapolation.

Cyclic voltammetry current against potential measurements were performed in order to study the corrosion behaviour of the materials. Cyclovoltammetric profilings of the powder supported electrodes, here (e.g., $Mo_5Rh_1Te_8$) (Fig. 4(a)) were made with different positive potential ranges. It was found that corrosion of the materials occurs when the applied electrode potential exceeded the open circuit potential value ($E > U_{ocp}$). At $E < U_{ocp}$ the electrodes were electrochemically stable. The open circuit potential, U_{ocp}, and thus the onset of anodic current, varies from compound to compound, see Table 2. Considering that the chalcogenide is more stable than molybdenum in the cluster matrix, the anodic dissolution of Chevrel phases with water can be represented by Equation 1:

$$Mo_{6-x}M_xTe_8 \longrightarrow Mo_{(6-x)z}M_xTe_8 + zMo^{3+} + ze^- \qquad (1a)$$

$$zMo^{3+} + yH_2O \leftrightarrow Mo_zO_y + 3ze^- + 2yH^+ \qquad (1b)$$

If $z = 1$ and $y = 3$, MoO_3 is the oxidation product

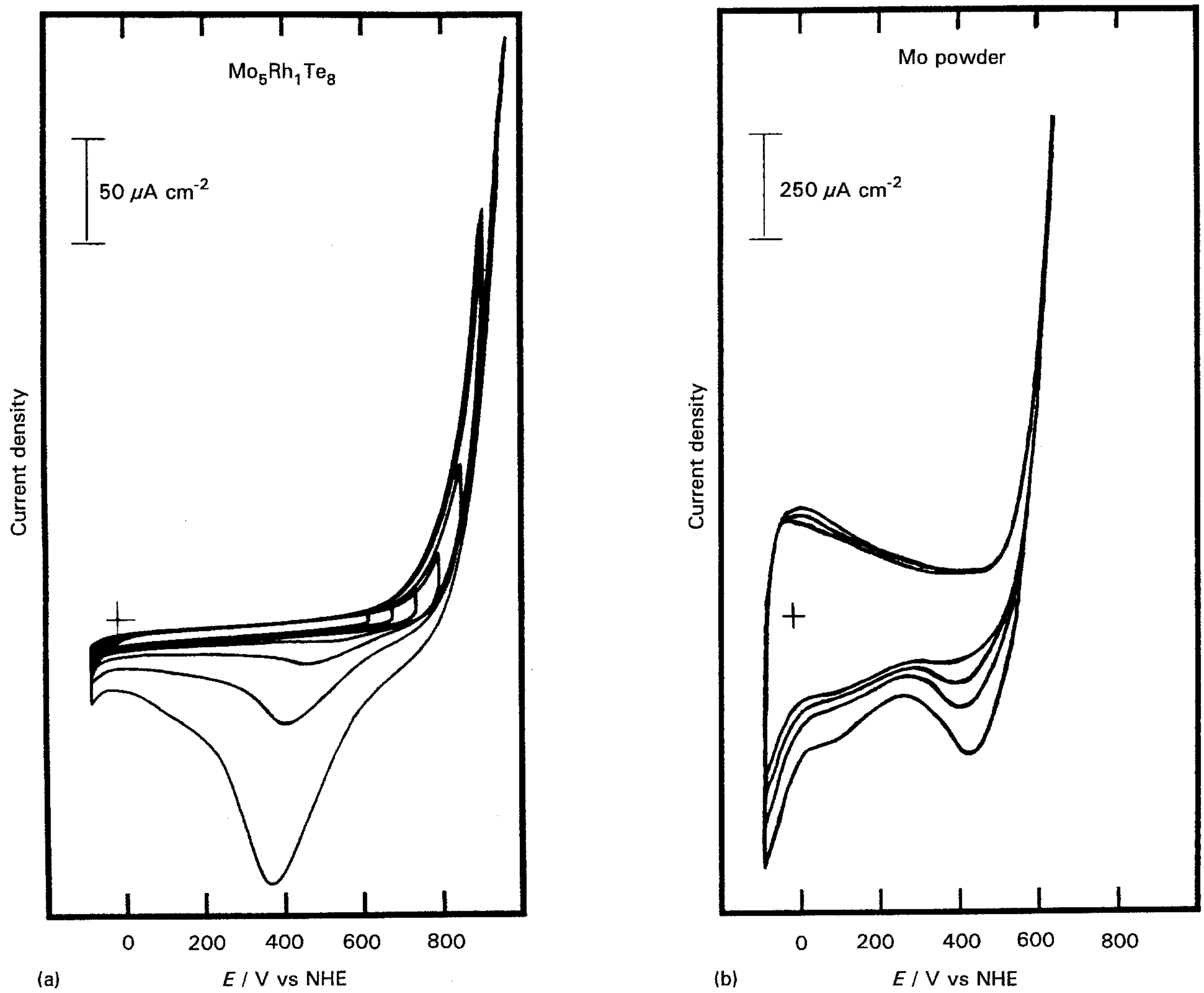

Fig. 4. Cyclic voltammetry current against potential profiles with different potential ranges of (a) $Mo_5Rh_1Te_8$ (U_{ocp} = 690 mV) and (b) molybdenum powder electrodes supported on carbon paste matrix, measured in N_2-saturated 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}.

remaining on the electrode surface whose reduction is detected when scanning anodically, cf. Fig. 4(a). Hence, Reaction 1(b) may describe the mixed electrode potential which controls the electrode open circuit potential, U_{oc}, in oxygen saturated electrolyte. Its thermodynamic potential is 0.317 V [9]. The U_{oc} values of all phases, see Table 2, are more positive than the thermodynamic one reflecting the kinetic stability of the cluster compounds.

Pure molybdenum powder electrodes prepared in the same way (Fig. 4(b)) revealed that for all Chevrel-phase materials molybdenum oxidizes according to a similar corrosion process. The magnitude of the C_{dl} after such an anodic oxidation was of the order of 100 to 250 μF cm^{-2} as a consequence of a corrosion-induced surface increase via formation of molybdenum oxide MoO_3. The electrochemical formation of molybdenum trioxide onto $Ru_2Mo_4Se_8$ and $Mo_2Re_4Se_8$ after positive polarization has been confirmed by XPS-investigations [7, 10].

Electrochemistry of $Mo_{4.2}Ru_{1.8}Se_8$ in aprotic electrolyte with low water content showed, that under these conditions no mixed potential occurred. Compared to measurements in sulphuric acid, the electrode could be essentially stabilized [6]. The catalytic properties of the material with respect to oxygen reduction in acetonitrile was reported to be the same as for platinum measured under the same conditions. It is therefore likely that inhibition of corrosion reactions took place due to absence of water. The open circuit potentials of the respective tellurides were more positive in an aprotic electrolyte and the materials could be polarized to higher positive potential.

The variation of the lattice constants (Table 1) as a function of NEC is in good agreement with measurements of pseudobinary phases where it was found that the increase in the number of electrons and thus the filling of binding valence band states, leads to a contraction of the cluster [11, 12]. This produces a kinetic stabilization of the compound during interfacial reaction and electrocatalysis.

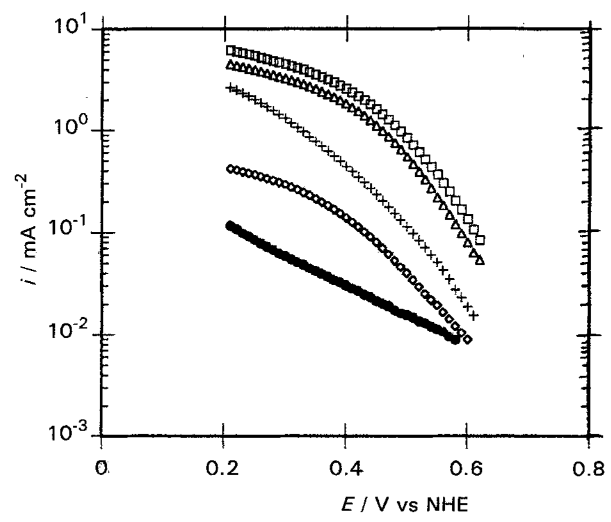

Fig. 5. Corrected mass transfer Tafel plot for oxygen reduction of cluster supported electrodes (Chevrel phases) in O_2-saturated 0.5 M H_2SO_4 (pH 0.3, data averaged from various measurements). Key: (□) $Mo_5Rh_1Te_8$; (△) $Mo_4Ru_2Te_8$; (+) $Mo_{5.8}Pt_{0.2}Te_8$; (◇) $Mo_{5.4}Os_{0.6}Te_8$; (●) Mo_6Te_8.

Kinetic studies of oxygen reduction electrocatalysis were performed with rotating disc electrodes (RDE) in O_2-saturated electrolyte. Before and after the experiments the open circuit potentials were measured. The corrected mass transfer Tafel plot ($\log i/E$), Fig. 5, shows that phases with mixed clusters are more electrocatalytic for oxygen reduction than the binary compound. This is assumed to be due to the more polar metal–metal bond in the clusters and to the presence of distinct adsorption sites. The Tafel behaviour is independent of the rotation frequency and covers the range 100 to 2500 rpm. From heterogeneous catalysis, it is known that the bimetallic interaction is a precondition for reaction selectivity supporting a defined catalytic process [13]. In the case of Chevrel phases with mixed clusters one could imagine that molybdenum in combination with (for example) Rh or Ru atoms are sustaining a cooperative effect, that is, that adsorption and desorption are occurring at distinct sites but with a system where electrons are delocalized to permit any exchange. Therefore, efficient oxygen reduction electrocatalysis must include, (for example) Rh or Ru cluster centres to produce water. Experimental evidence already exists with new phases with a low molybdenum content [14] investigated with in situ EXAFS spectroscopy [15].

The overpotential η was determined by extrapolation with a current density of 10^{-5} A cm^{-2} with respect to thermodynamic potential $E_0(O_2/H_2O) =$ 1.21 V (pH 0.3). Compared to Mo_6S_8 and Mo_6Se_8 [5, 16] the Mo_6Te_8 reveals with $\eta = 650$ mV the lowest overvoltage for oxygen reduction among the binary Chevrel phases. As can be seen from Fig. 6, the electronic properties strongly influence the electrocatalytic behaviour: with increasing NEC the overvoltage decreases significantly. Certainly, the effect of the substituted metal itself should not be neglected. Considering pure transition metals, Pt reveals the highest catalytic activity ($\eta = 260$ mV [17]) while Rh (600 mV) and Ru (550 mV) are comparably poor catalysts [17]. Further, it should be taken into

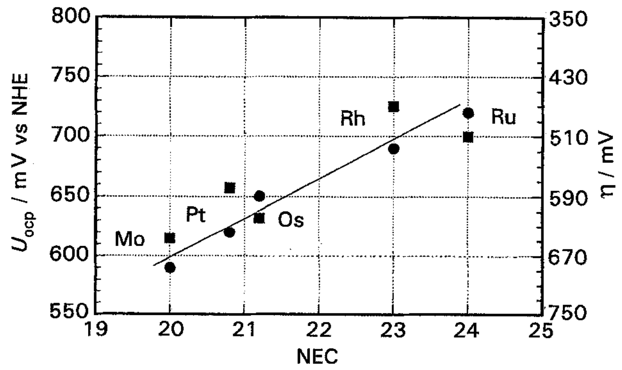

Fig. 6. Dependence of the open circuit potential U_{ocp} (●) and oxygen overvoltage η (■) at a current density of 10^{-5} A cm^{-2}, in O_2-saturated H_2SO_4 of several molybdenum cluster tellurides (Chevrel phases) as a function of their number of electrons per cluster (NEC).

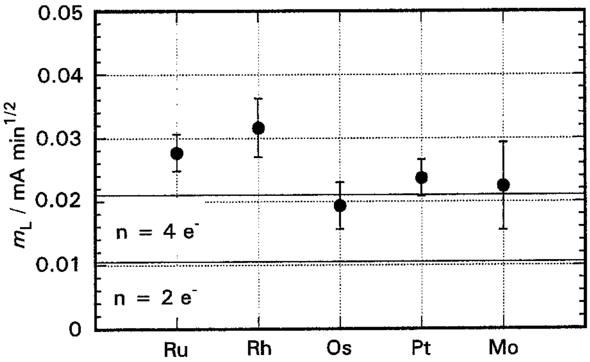

Fig. 7. Mean Levich-slopes, m_L, of Chevrel phase powder electrodes. The two lines indicate an overall electron transfer for $n = 2$ and $n = 4$ electrons. (Data calculated from the Levich equation, using the following parameters. Oxygen concentration $C_{O_2} = 1.1 \times 10^{-6}\,\mathrm{mol\,cm^{-3}}$, diffusion coefficient $D_{O_2} = 1.4 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$, kinematic viscosity $\nu = 0.01\,\mathrm{cm^2\,s^{-1}}$ (from [18]), geometrical electrode surface $A = 0.196\,\mathrm{cm^{-2}}$).

account that in the case of pseudobinary phases $Mo_{6-x}M_xTe_8$, NEC is not independent of the degree of substitution x. To study the influence of x on the electrocatalytic properties, a whole series of phases with the same pseudobinary metal M and various degrees of substitution should be synthesised and investigated. The degree of substitution reported here was the highest that could have been reached. In most cases multiphase products were the main product.

The resulting Tafel parameters (current exchange density, i_0 and Tafel slope, b) and oxygen reduction overpotentials are also listed in Table 2. Except for Mo_6Te_8, the values for the Tafel slopes b are all about $-120\,\mathrm{mV\,(decade)^{-1}}$. The higher Tafel slope of the binary phase, $-305\,\mathrm{mV\,(decade)^{-1}}$, might strongly indicate that a deviation of the kinetics of molecular oxygen reduction is due to its adsorption on molybdenum centres. This phenomenon is to some extent diminished on the substituted cluster compounds.

The overall electron transfer was estimated through the Levich slopes, m_L, and compared to the calculated slopes using data from the literature, Fig. 7. As can be seen, the experimental Levich slopes, m_L, of all compounds investigated are around the theoretical one ($0.021\,\mathrm{mA\,min^{1/2}}$), calculated by Equation 2 for $n = 4$ electron transfer (water production).

$$m_L = \left(\frac{2\pi}{60}\right)^{1/2} \times 0.62 \times 10^3 nFC_{O_2}\nu^{-1/6}D_{O_2}^{2/3}A \quad (2)$$

where the symbols have their usual meaning, see legend of Fig. 7 for parameters used.

These results are supported by studies carried out using the rotating ring disc electrodes (RRDE) technique on mixed cluster selenides [7] where the hydrogen peroxide formation was lower than 5%.

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