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(54) **ELECTROCHEMICAL CELL FOR THE OXIDATION OF ORGANIC COMPOUNDS, AND ELECTROCATALYTIC OXIDATION PROCESS**

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(57) **ABSTRACT**

An electrochemical cell comprising a negative electrode, a solid electrolyte which conducts oxygen ions, and a positive electrode comprising zeolites, mordenites, silicates, phosphates or mixed-metal oxides having a pore size of less than 200 nm can be used in a process for partially oxidizing organic compounds, for example alkanes, olefins or aromatic compounds.

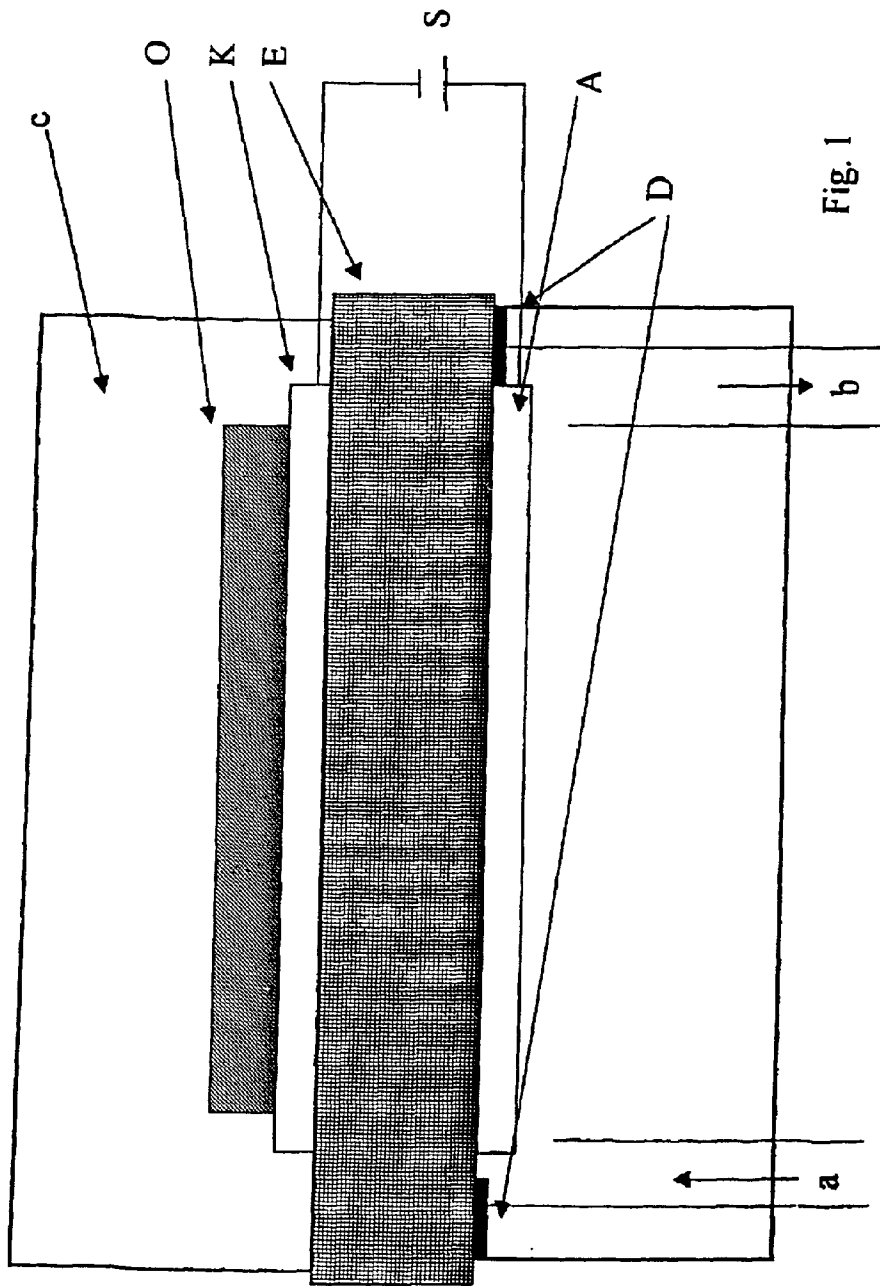


Fig. 1

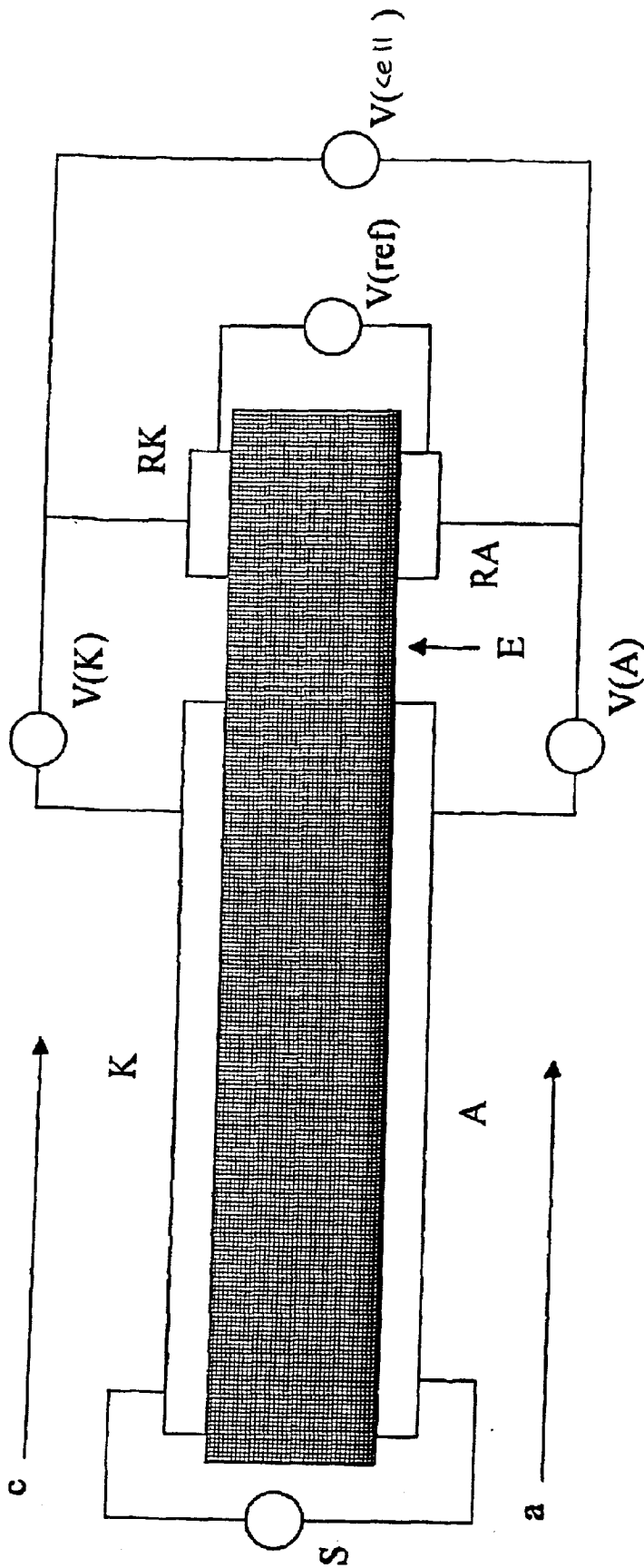


Fig. 2

ELECTROCHEMICAL CELL FOR THE OXIDATION OF ORGANIC COMPOUNDS, AND ELECTROCATALYTIC OXIDATION PROCESS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The invention relates to an electrochemical cell and to an electrochemical, catalytic oxidation process for preparing selectively oxidized organic compounds.

[0003] 2. Discussion of the Background

[0004] The direct selective oxidation of organic compounds has until now rarely been possible because the partially oxidized product produced thereby is usually more reactive than the starting materials employed, resulting in complete oxidation of the starting materials to form, ultimately, carbon dioxide. An exception to this usual rule is the direct oxidation of n-butane to provide maleic anhydride, but in this case, stabilization of the oxidation product by cyclization plays a crucial role. In particular, the problem of how to directly oxidize alkanes and aromatic compounds has not been satisfactorily resolved to-date.

[0005] Many attempts have been made to develop novel heterogeneous catalysts for the partial direct oxidation of unreactive organic compounds. However, the yield of the partially oxidized product using such catalysts is usually too low to be industrially useful.

[0006] By contrast, little attention has been paid to partially oxidizing organic compounds by electrochemical methods. On the contrary, the forefront of development work in this area is in the area of total oxidation of suitable compounds in fuel cells for the production of electrical energy.

[0007] U.S. Pat. No. 4,329,208 describes the electrochemical oxidation of ethene to ethylene oxide using a positive electrode consisting of silver or a silver alloy and a solid electrolyte system comprising zirconium oxides.

[0008] U.S. Pat. No. 4,661,422 describes another process for electrochemically oxidizing organic compounds, in which hydrocarbons were oxidized at a metal/metal oxide positive electrode using a molten salt electrolyte. The molten salt comprises carbonate, nitrate or sulfate salts, and the negative electrode is made of mixed oxides of metals from groups IB, IIB, IIIA, VB, VIB, VIIB and VIIB of the Periodic Table.

[0009] Takehira et al., in *Catalysis Today*, 1995, 25, 371, have investigated the partial oxidation of propene in an apparatus similar to fuel cells, using a Y-stabilized ZrO₂ electrolyte, a Au supported Mo/Bi mixed catalyst positive electrode material, and a Ag negative electrode material. The reaction temperature was 475° C.

[0010] In each case, the yield of the desired oxidation product is generally so low that none of these processes are industrially useful, and in addition, the problem of the total oxidation of the organic substrate to carbon dioxide has not yet been solved. In addition, the electrolyte acts as "oxygen pump", i.e. the oxygen needed for the oxidation is reduced at the negative electrode and then migrates in ionic form through the electrolyte to the positive electrode. The positive electrode space contains only the substrate to be oxidized

and possibly an inert gas. Even if oxygen is fed into the positive electrode space, the yield of the desired oxidation product does not increase.

[0011] Another disadvantage of the above-described electrochemical partial oxidations is that the reaction temperature is determined by the oxygen conductivity of the electrolyte. The electrolytes employed only have sufficient oxygen conductivity at temperatures significantly above the optimum temperatures for such oxidation reactions, which undoubtedly, at least in part, explains why such process show low selectivity.

[0012] In particular, processes which employ molten salt electrolytes invariably have such high reaction temperatures (up to 750° C.) that it is difficult to avoid decomposing the oxidation products. In addition, such processes are not suitable for preparing thermally unstable compounds (for example Michael systems).

[0013] The discovery of the NEMCA (Non Faradaic Electrochemical Modification of Catalytic Activity) effect opens up the possibility of developing more economical electrochemical processes. Vayenas et al. in "Studies in Surface Science and Catalysis", R. K. Grasselli, S. T. Oyama, A. M. Gaffney, J. E. Lyons (Editors), 110, 77 (1997) and *Science* (1994), 264, 1563, describe an electrochemical process based on a conductive, porous metal oxide film on a solid electrolyte, such as, for example, ZrO₂ stabilized by Y. In this process, gas-tight separation of the positive electrode and negative electrode spaces is not required, and the oxidant can be fed concomitantly into the positive electrode space. However, carbon dioxide is still produced by the total oxidation of the substrate, and the selectivity of the oxidation reactions to produce a desired, partially oxidized product is very low, even at low conversions.

SUMMARY OF THE INVENTION

[0014] The object of the present invention is to provide an electrochemical cell for selectively oxidizing organic compounds and a process for selectively oxidizing organic compounds using this cell.

[0015] Surprisingly, it has been found that an electrochemical cell consisting of a negative electrode, a solid electrolyte which conducts oxygen ions, and a positive electrode coated or comprising a catalytically active compound is highly suitable for the selective oxidation of organic substrates.

BRIEF DESCRIPTION OF DRAWINGS

[0016] FIG. 1 is a diagram of an exemplary electrochemical cell according to the present invention.

[0017] FIG. 2 is a diagram of a test apparatus for optimizing operating conditions of an electrochemical cell according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] In a first embodiment, the present invention provides an electrochemical cell consisting of a negative electrode, a solid electrolyte which conducts oxygen ions, and a positive electrode comprising a positive electrode material comprising zeolites, mordenites, silicates, phosphates or

mixed metal oxides with a pore size of below 200 nm. In a second embodiment, the positive electrode material of the electrochemical cell is a coating on the solid electrolyte. In a third embodiment, the positive electrode material of the electrochemical cell is coated on a conventional metal electrode. In a fourth embodiment, the positive electrode of the electrochemical cell further comprises a mixture of the solid electrolyte positive electrode material. In a fifth embodiment, the positive electrode of the electrochemical cell further comprises a mixture of an electrically conductive metal and the positive electrode material. In a sixth embodiment, an organic compound is partially or selectively oxidized using an electrochemical cell according to the present invention.

[0019] The negative electrode of the electrochemical cell of the present invention may be a metal, such as copper, gold, silver, platinum or iridium, or mixtures of these metals, one or more metal oxides or a mixed metal oxide. For the purposes of the present invention, the term "mixed oxides" includes multi-metal oxide materials as well as mixtures of metal oxides. Multi-metal oxide materials are metal oxides in which two or more metals occupy lattice sites in the oxide structure. In any case, phase transitions are possible, depending on the stoichiometry of the mixed oxide and how they are heat treated.

[0020] In addition, the negative electrode may comprise perovskites of the general formula I



[0021] where

[0022] X^{13} =Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu,

[0023] X^{14} =Ca, Sr, Ba and/or Mg,

[0024] X^{15} =Mn, Fe, Ti, Ga, Mn and/or Zr,

[0025] X^{16} =Co, Ni, Cu, Al and/or Cr

[0026] $u=0$ to 1.2,

[0027] $v=0$ to 1.0

[0028] $w=0.01$ to 0.8,

[0029] with the proviso that $u+v+w$ is ≤ 1.5 , and

[0030] $x=0.2$ to 1.3,

[0031] $y=0$ to 0.9,

[0032] with the proviso that $x+y$ is ≥ 0.3 .

[0033] The number of oxygen atoms ($3+z$) is defined by the valency and amount of the elements other than oxygen in the oxide.

[0034] German patent 197 02 619 C1 describes the preparation of negative electrode materials for high-temperature fuel cells composed of non-stoichiometric perovskites of the formula $\text{L}_a\text{M}_b\text{Mn}_x\text{Co}_8\text{O}_3$. However, fuel cells are designed for the production of electrical energy by means of total oxidation of a substrate, rather than the partial oxidation of a substrate (e.g., an organic compound).

[0035] The composition of the solid electrolyte which conducts oxygen ions is has a significant effect on the conductivity of the electrochemical cell. The conductivity of the solid electrolyte may be drastically increased depending

on both the composition and geometry of the electrolyte, in particular the layer thickness of the solid electrolyte. Preferred electrolyte layer thicknesses are less than 200 μm , more preferably less than 150 μm , most preferably less than 60 μm .

[0036] The solid electrolyte which conducts oxygen ions in the electrochemical cell of the present invention may, for example, consist of cerium oxide (CeO_2), or cerium oxide stabilized with any of lanthanum oxide (La_2O_3), yttrium oxide (Y_2O_3), ytterbium oxide (Yb_2O_3) and/or gadolinium oxide (Gd_2O_3). It is furthermore possible to employ a solid electrolyte consisting of zirconium oxide (ZrO_2), or zirconium oxide stabilized with any of calcium oxide (CaO), scandium oxide (Sc_2O_3), yttrium oxide (Y_2O_3) and/or ytterbium oxide (Yb_2O_3). In the simplest embodiment, the solid electrolyte which conducts oxygen ions contains a metal or metal oxide or complex mixed-metal oxides, as shown below.

[0037] In addition to mixing metal powders or flakes, for example copper, silver, gold, platinum, palladium and iridium, in the solid electrolyte, it is also possible to arrange a metal foil, preferably an oxygen-permeable metal foil, between the electrolyte and the positive electrode. Metal foils of this type may consist of a metal of high electrical conductivity, such as copper, silver, gold, platinum, palladium, iridium or a mixture of these metals. The thickness of these metal foils should be less than 200 μm , preferably less than 100 μm , more preferably less than 50 μm .

[0038] The layer thickness of the solid electrolyte may be modified by various methods or the conductivity may be improved by, for example, by CVD (i.e., chemical vapor deposition), PVD (i.e., physical vapor deposition), spin rotation or MOD spin casting (Swider, Karen Elizabeth, Univ. Pennsylvania, Philadelphia, Pa., USA. Avail. Univ. Microfilms Int., Order No. DA9308667. (1992); 242 PP: From: Diss. Abstr. Int. B 1993, 53 (11), 5927), tape casting (Plucknett, Kevin P.; Caceres, Carlos H.; Wilkinson, David S.; Department of Materials Science Engineering, McMaster University, Hamilton, ON, Can.; J. Am. Ceram. Soc. (1994), 77(8), 2137-44), slip casting (Forthmann, R.; Blass, G.; Buchkremer, H. -P. Forschungszentrum Julich GmbH, Julich, Germany. Editor(s): Sarton, L. A. J. L.; Zeedijk, H. B.; Mater., Funct. Des., Process. Eur. Conf. Adv. Mater. Processes Appl., 5th (1997), 3 3/271-31274. Publisher: Netherlands Society for Materials Science; Zwijndrecht, Neth.) or especially by the MOCVD method (i.e., metal-organic chemical vapor deposition). This method allows membrane thicknesses, or in the present case, electrolyte layer thicknesses, of between 1 μm and 50 μm to be obtained through decomposition on a porous substrate. The method has been described by O. Gorbenko, A. Kaul, A. Molodyk, V. Fuflygin, M. Novozhilov, A. Bosak, U. Krause, G. Wahl in "MOCVD of perovskites with metallic conductivity", Journal of Alloys and Compounds, 251 (1997), 337-341. All of the above-noted references describing various methods of preparing thin layers are herein incorporated by reference. Experimental problems, such as stoichiometric deviation, loss of alkali metal and alkaline earth metal compounds in the film and the formation of cracked products can be solved through a suitable choice of the starting stoichiometry and through the choice of the decomposition conditions.

[0039] Suitable substrates for these membrane or electrolyte layers are aluminum oxide (Al_2O_3), lanthanum calcium manganate ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) and calcium stabilized zirconium ($\text{Zr}_{1-x}\text{Ca}_x\text{O}_2$).

[0040] In a particular embodiment of the present invention, the solid which conducts oxygen ions is a perovskite of the general formula II



[0041] where

[0042] $\text{Ln}=\text{La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ and/or Lu

[0043] $\text{X}^1=\text{Ca, Sr, Ba}$ and/or Mg

[0044] $\text{X}^2=\text{Ga, Al, Mn, Ti, Nb, Y, W}$ and/or Zr

[0045] $\text{X}^3=\text{Fe, Co, Ni}$ and/or Cu

[0046] $a=0.1$ to 0.9 ,

[0047] $b=0.1$ to 0.9 ,

[0048] $c=0$ to 0.9 ,

[0049] $d=0$ to 0.9

[0050] with the proviso that $a+b=0.3$ to 1.5 .

[0051] The number of oxygen atoms e is determined by the valency and amounts of the elements other than oxygen in this formula.

[0052] In a further embodiment, the solid which conducts oxygen ions is a pyrochloro compound of the general formula III



[0053] where

[0054] $\text{Ln}=\text{La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ and/or Lu

[0055] $\text{X}^4=\text{Na, Mg, Ca}$ and/or Sr,

[0056] $\text{X}^5=\text{Ti, Nb, Ta}$ and/or Zr,

[0057] $\text{X}^6=\text{Fe, Al, Sc, Ga}$ and/or Y,

[0058] $f=0.2$ to 1.2 ,

[0059] $g=0$ to 0.8 ,

[0060] $h=0.2$ to 1.2 ,

[0061] $i=0$ to 0.8 .

[0062] The number of oxygen atoms k is again determined by the valency and amount of the elements other than oxygen in this formula.

[0063] These compounds can be prepared, for example, by a sol-gel process (Shag Zonping; Sheng, Shishan; Chen, Hengrong; Li, Lin; Pan, Xiulian; Xiong Guoxing; State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, Peop. Rep. China. Gongneng Cailiao (1998), 29 (Suppl), 1091-1093, 1096), spray drying (Sizgek, E.; Bartlett, J. R.; Brungs, M. P. Materials Division, Australian Nuclear Science and Technology Organisation, Menai, Australia. J. Sol-Gel Sci. Technol. (1998), 13 (1/2/3), 1011-1016 or drip pyrolysis (P. Gordes et al., Den. J. Mater. Sci. (1995), 30 (4), 1053-8) or decomposition methods (for example: N. Dhas et al., India J. Mater. Chem. (1993), 3 (12), 1289-1294, or D. Fumo et al., Port. Mater Res. Bull. (1997), 32 (10), 1459-1470), each of which is herein incorporated by reference.

[0064] The positive electrode of the electrochemical cell of the present invention may consist entirely or in part of mixed oxides of formula V (described hereinafter) or consist of a conventional metal electrode, for example platinum, gold, silver, copper, iridium, palladium or alloys of these metals, coated with an undoped or metal-doped zeolites, such as, for example, mordenites, ZSM-5 or ZSM-11. Titanium silicates, such as, for example, TS-1, are also suitable for the positive electrode coating. Catalytically active materials of this type are described comprehensively in "Technische Katalyse" (Industrial Catalysis) (Jens Hagen), VCH Verlagsgesellschaft mbH, D-6951 Weinheim, 243-267 (1996), herein incorporated by reference. Amorphous microporous mixed-metal oxides, as described, for example, in DE 195 06 843, herein incorporated by reference, are also suitable as coating materials for the positive electrode. In addition, catalysts of the composition disclosed in DE 198 54 615, herein incorporated by reference, metal-doped zeolites, silicates, aluminum silicates and aluminum phosphates, are also suitable coating materials for the positive electrode. In each case, it is essential that the pore size of these positive electrode coating materials is less than 200 nm, preferably less than 100-nm, in particular less than 20 nm, preferably less than 10 nm, very particularly less than 1 nm.

[0065] Preferred positive electrode materials for the electrochemical cells of the present invention may consist of a compound of formula IV



[0066] where

[0067] $\text{E}=\text{an element from group IA, IIA, IIIA, IVA or VA or IIIB, IVB, VB, VIB, VIIB or VIII of the Periodic Table of the Elements}$

[0068] $\alpha=\text{from } 0 \text{ to } 0.1$

[0069] $\beta=\text{from } 0 \text{ to } 0.1$,

[0070] with the proviso that α and β are not simultaneously 0.

[0071] e is determined by the valency and frequency of the elements other than oxygen in formula IV. In a preferred embodiment, $\alpha=\text{from } 0 \text{ to } 7 \cdot 10^{-2}$ and $\beta=\text{from } 0.1 \text{ to } 10^{-5}$.

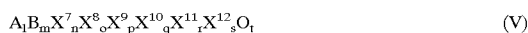
[0072] In practice, a film of the positive electrode materials, in particular the mixed oxides, may be first applied to the solid electrolyte, for example by screen printing, and then bonding the mixed oxide positive electrode material directly to the solid electrolyte by heating. An example of this technique is given in JP 09 239 956, herein incorporated by reference.

[0073] The positive electrode materials may also be sintered onto a conventional metal electrode in amounts of at most 300% by weight (based on the weight of the conventional metal electrode), in particular at most 200% by weight, preferably at most 100% by weight, at temperatures of at most 1500° C., in particular at temperatures of at most 900° C., preferably at temperatures of at most 750° C. The heat stability of these coatings is critical. Thus, for example, zeolites are substantially stable even at temperatures of above 1000° C. However, the coatings can also be grown onto the surface of the conventional metal electrode and allowed to crystallize, for example by crystallizing the

desired mesoporous, microporous or nanoporous catalytically active layer onto a conventional metal electrode. This procedure may be analogous to the crystallization of, for example, a zeolite layer on the surface of a support (e.g., U.S. Pat No. 4,800,187, incorporated herein by reference). Alternatively, as described above, the positive electrode materials of the present invention may be coated directly onto the solid electrolyte.

[0074] An additional possible method for crystallizing, for example, a zeolite layer on the surface of a mesoporous support or, in the present case, on the surface of a conventional metal electrode or positive electrode is the crystallization of zeolite grafts within the pores of a monolithic support (U.S. Pat No. 4,699,892, FR 94-5562 and WO 95/29751, each of which is herein incorporated by reference).

[0075] A suitable positive electrode material or positive electrode coating, i.e. catalytically active coating, is also a mixed oxide of the general formula V



[0076] where

[0077] A and B are an element from Group IA, IIA and/or VA and/or Group IVB, VB, VIB, VIIIB, or VIII of the Periodic Table of the Elements

[0078] $X^7 = V, Nb, Cr, W, Ta, Ga$ and/or Ce

[0079] $X^8 = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr$ and/or Ba,

[0080] $X^9 = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cu, Ag, Au, Pd$ and/or Pt,

[0081] $X^{10} = Fe, Co, Ni$ and/or Zn,

[0082] $X^{11} = Sn, Pb, Sb$ and/or Te,

[0083] $X^{12} = Ti, Zr, Si$ and/or Al, where

[0084] $l = 0.001$ to 30,

[0085] $m = 0.001$ to 20,

[0086] $n = 0$ to 15,

[0087] $o = 0.001$ to 10,

[0088] $p = 0$ to 10,

[0089] $q = 0$ to 40

[0090] $r = 0$ to 10 and

[0091] $s = 0$ to 80, with the proviso that $l+m$ is ≥ 0.01 and $l+o$ is ≥ 0.005 .

[0092] The number of oxygen atoms t is determined by the valency and amount of the elements other than oxygen in this formula.

[0093] As described above, and for the purposes of the present invention, the term "mixed oxides" includes multi-metal oxide materials as well as mixtures of metal oxides, where multi-metal oxide materials are metal oxides in which two or more metals occupy lattice sites in the oxide structure. In any case, phase transition are possible, depending on the stoichiometry of the mixed oxides, and how they are heat treated.

[0094] Mixed oxides as described above are known from other technical areas and may be employed, for example, as heterogeneous catalysts for gas-phase reactions. The preparation and use of such compounds is described, for example, in EP 0 417 723, herein incorporated by reference. While it is known that mixed oxides of this type may be used as heterogeneous catalysts in non-electrolytic chemical reactions, the use of such mixed oxides as a positive electrode material in electrochemical processes, according to the present invention, is not described in the literature.

[0095] Inter alia, the following mixed oxides, for example, may be suitable for the electrochemical process of the present invention:

[0096] a) $Mo_{0.57}Bi_{0.86}Fe_{6.4}Co_{3.2}K_{0.05}$ oxide

[0097] b) $Mo_{12}Bi_{0.5}Fe_4Co_8Ca_{0.1}K_{0.1}$ oxide

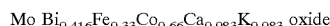
[0098] c) $Mo_{12}Bi_5Fe_4Co_8Ca_{0.1}K_{0.1}$ oxide

[0099] d) $Mo_{12}Bi_{0.98}Ni_{8.29}Fe_{1.95}Si_{10}K_{0.05}Na_{0.15}$ oxide

[0100] e) $Mo_{12}Bi_4Si_3Ni_3Co_{1.9}Cu_{0.26}Fe_{0.1}$ oxide

[0101] f) $Mo_{12}Bi_4Si_3Ni_3Fe_{1.9}Cu_{0.26}Co_{0.1}$ oxide

[0102] Empirical formulae data for said mixed oxides may also be described using smaller indices in the empirical formula. For example, the empirical formula of mixed oxide c), i.e., $Mo_{12}Bi_5Fe_4Co_8Ca_{0.1}K_{0.1}$ oxide can also be divided by the number 12 to give the empirical formula:



[0103] Both empirical formulae describe the same mixed oxide. This means that in many cases the oxide composition may be definitively described only by the ratio of the components present therein.

[0104] The positive electrode may be composed entirely or only partly of the mixed oxides of the formula V. In general, a conventional metal electrode, for example made of platinum, gold, silver, copper, iridium, palladium or alloys of these metals, may also be provided with a surface comprising these mixed oxides. It is likewise possible for the catalytically active mesoporous, microporous or nanoporous positive electrode coating to be sintered or allowed to crystallize directly onto a metallic electrode.

[0105] It is likewise possible to mechanically mix a conductive metal, such as, for example, copper, silver, gold, platinum, palladium or iridium, with the positive electrode material—for example if mixed oxides are present—in order to improve the conductivity of the coating material. However, since pure metals may chemically react during the sintering process, the solid electrolytes of formula II or III, preferably a perovskite or cerium oxide, more preferably a stabilized perovskite or cerium oxide, is usually mechanically mixed with the positive electrode material in order to increase the conductivity of the positive electrode.

[0106] The electrochemical cells and processes of the present invention allow the partial or selective oxidation of organic compounds, for example saturated organic compounds, such as ethane, propane, isobutane, butane, hexane, pentane, cyclohexane, vinylcyclohexane, octane and cyclododecane, or compounds containing triple bonds, such as, for example, ethyne, propyne or butyne. In addition, these hydrocarbons may also be used as starting materials to

prepare synthesis gas, i.e. hydrogen plus carbon monoxide using the electrochemical cell and process of the present invention.

[0107] Furthermore, olefins or compounds containing double bonds and aromatic compounds, such as, for example, ethene, propene, butene, isobutene, hexene, cyclohexene, vinylcyclohexene, cyclooctene, cyclododecene, butadiene, isoprene, pentadiene, hexadiene, cyclooctadiene, cyclododecatriene and benzene, toluene, ortho-xylene, meta-xylene, para-xylene, cumene, cumylbenzene, cyclododecylbenzene, 2-n-butylbenzene, ethylbenzene, tert-butylbenzene, tert-butyltoluene, methoxytoluene and phenoxymethyltoluene, or derivatives thereof, may be oxidized to the corresponding epoxides, hydroxyl compounds, aldehydes and ketones, and carboxylic acids using the electrochemical cell and process of the present invention.

[0108] Alcohols, ketones and aldehydes may be converted selectively into the corresponding aldehydes or carboxylic acids, with chain cleavage where appropriate. Examples thereof include trimethylcyclohexanol (from trimethylcyclohexane), cyclododecanol (from cyclododecane), acrolein (from propane or propene), methacrolein (from isobutane or isobutene) and cyclododecanone (from cyclododecane). Thus, by partial or selective oxidation, we mean that the organic compound used as a starting material in the process of the present invention is not completely oxidized to carbon dioxide, but rather is oxidized to an intermediate level.

[0109] In the electrochemical cell of the present invention, oxygen is taken up by the negative electrode and passed to the positive electrode through the solid electrolyte. The negative electrode can also be exposed to a stream of air or an oxygen-containing off-gas stream. It is important that this gas stream contains a gas which can be ionized, such as oxygen, which can then migrate through the solid electrolyte to the positive electrode.

[0110] The organic compound to be oxidized (i.e., the organic starting material) can be mixed with air and/or oxygen and/or an inert gas, such as, for example, nitrogen, and passed over the positive electrode. The organic starting material may be introduced in gaseous or liquid form, but introducing the organic starting material in the gaseous form is preferred, and has provided good results at the reaction temperatures of the present invention. Thus, it benzene or benzene derivatives, together with dinitrogen monoxide (i.e., N_2O) and/or air or oxygen containing dinitrogen monoxide or another off-gas containing dinitrogen monoxide, for example from the synthesis of adipic acid, may be oxidized in the electrochemical cell of the present invention, thereby forming phenol or derivatives thereof.

[0111] The present invention also relates to a process for electrochemically oxidizing organic compounds, in which organic compounds are introduced into the positive electrode side of an electrochemical cell consisting of a negative electrode, a solid electrolyte which conducts oxygen ions, and a positive electrode which has a coating of zeolites, mordenites, silicates, phosphates or mixed-metal oxides having a pore size of less than 200 nm, and a gas containing oxygen or N_2O is introduced into the negative electrode side.

[0112] The electrochemical oxidation of organic compounds by the process of the present invention or in the electrochemical cell of the present invention is carried out at elevated temperatures, preferably from 100 to 650° C., particularly preferably from 200 to 550° C.

[0113] The process of the present invention may also be carried out at elevated pressures, for example at pressures of up to at most 100 bar, preferably from 1 to 20 bar, more preferably at about 10 bar.

[0114] In the process and electrochemical cell of the present invention, oxygen is ionized at the negative electrode and moves through the negative electrode to the positive electrode. The oxygen is activated at the positive electrode in such a way that it reacts with the organic compound passed over the positive electrode. The oxygen feed stream can also move through a porous, non-gas-tight solid electrolyte. The gas stream in the positive electrode space may also contain an inert gas in addition to the organic compound substrate (i.e., the compound to be oxidized) and oxygen.

[0115] An example of the structure of an electrochemical cell of the present invention which may be used to carrying out the process of the present invention is shown in **FIG. 1**.

[0116] The negative electrode K and the positive electrode A are joined to the electrolyte E which conducts oxygen ions, for example by a heat treatment, so that a current-conducting connection is provided therebetween. The two electrodes are supplied with current via a voltage source S.

[0117] The starting material and oxygen are introduced as gas stream a) to the positive electrode A, and the resultant product gas b) is transported away either by the positive pressure of the gas stream a) or by means of a corresponding reduced pressure. The gas stream c) on the negative electrode side of the electrochemical cell may comprise air, oxygen or another oxygen-containing gas mixture, and after passing over the negative electrode, is depleted in oxygen.

[0118] The positive electrode space is sealed against the electrodes by gold foils D. The oxygen feed stream (at a pressure of about 10 kPa) is introduced to the electrochemical cell via the porous element O.

[0119] The electrochemical cell of the present invention may have any spatial arrangement of positive electrode, negative electrode and electrolyte, and is not restricted to flat plates or continuous layers. For example, the electrochemical cell of the present invention may be a tubular reactor, in which case, positive electrode and negative electrode materials are applied to a tube made from the electrolyte, and connected appropriately to a voltage source. Furthermore, the positive electrode or negative electrode layer may have the topography of a fabric or structured surface layer with regular recesses or elevations.

[0120] The experimental arrangement shown diagrammatically in **FIG. 2** may be used to determine or optimize the effects of the temperature, the gas flow rate, gas residence time and the current strength used in the process of the present invention, on the performance of the electrochemical cell. The current strength required generally depends on the size or product capacity of the electrochemical cell and is generally between 0 and 10 mA, preferably from 10 to 20 mA. A current source S which operates at a current strength

of from -100 to $+100$ mA, can be programmed for different flow rates. The excess voltage at the positive electrode A (V_A) the excess voltage at the negative electrode K (V_K), the measurement-cell voltage (V_{cell}) and the voltage V_{ref} of the reference electrodes RA and RK (which are usually made of platinum) may be monitored.

[0121] The current strengths described above relate to those used in a pilot plant scale electrochemical process, such as, for example, those shown in FIG. 2. When greater production capacities are desired, correspondingly higher current strengths are necessary. Industrial scale current strengths can be determined readily by simple preliminary experiments.

[0122] In FIG. 2, E denotes the solid electrolyte which conducts oxygen ions, a) denotes the starting-material gas stream (benzene→phenol), and c) denotes oxygen or an oxygen-containing gas.

[0123] Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only, and are not intended to be limiting unless otherwise specified.

EXAMPLES

[0124] Step a): Preparation of the solid electrolyte which conducts oxygen ions

[0125] aa) either commercially available cerium oxide (Indec b.v.) is used; or

[0126] ab) a suspension containing a binder (for example 16 g of ethylcellulose, Merck) and a solvent (e.g., 422 g of terpineol; i.e. p-menth-1-en-8-ol) is prepared with the desired compounds, for example, by mixing for 24 hours using a ball mill or bead mill (Netzsch). This suspension is cast as a thick film, which, after removal or evaporation of the solvent, provides a crude film of the electrolyte. The crude electrolyte film may then be cut to the desired size.

[0127] Depending on the electrolyte used ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_2$ and CeO_2 were used in the present experiment), it may be advantageous to use different layer thicknesses. For example, when the electrolyte is $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_2$, a layer thickness of about $80\ \mu\text{m}$ was used, while when the electrolyte was CeO_2 a layer thickness of $200\ \mu\text{m}$ was used. This electrolyte film may be sintered between two porous aluminum oxide plates at a temperature of 1500°C . for 6 hours (e.g., when the electrolyte film is $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_2$) or 1300°C . and 8 hours (e.g., when the electrolyte film is CeO_2).

[0128] Step b): Production of the negative electrode

[0129] ba) The negative electrode was either a platinum layer vapor-deposited onto the electrolyte; or

[0130] bb) as described in detail under c).

[0131] The composition of the negative electrode powder was $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (Rhône Poulenc), sintered for 1 hour at 1100°C .

[0132] Step c): Production of the positive electrode/catalytic layer

[0133] The desired molar ratios of the elements comprising the positive electrode/catalytic layer (except for molybdenum), in the form of their respective nitrate salts (Merck), were dissolved in about 50°C . warm water and stirred with a stainless steel paddle stirrer. Molybdenum, in the form of ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\times 4\text{H}_2\text{O}$ (for example from H. C. Starck), was initially dissolved separately.

[0134] The molar ratios of the elements are shown, for example, in the table for Examples 1 to 4 or by the formula IV.

[0135] The ammonium heptamolybdate, in an amount corresponding to the desired molar ratio, was then poured into the nitrate salt solution of the other elements, and stirred. A product initially precipitated, and then re-dissolved upon continued stirring, then gelled after a short time.

[0136] The gel was subsequently dried at 110°C . in a stream of air and calcined at 450°C . The resultant material was subsequently ground or used directly for the preparation of the catalytic paste.

[0137] The desired catalytically active compounds were converted into a paste with binder and solvent using a ball mill or a bead mill. This paste was then screen-printed onto the electrolyte. After removal or evaporation of the solvent, the entire cell was sintered at a temperature of 400°C ., thereby providing a catalytically active layer with a layer thickness of $50\ \mu\text{m}$, using the following detailed process:

[0138] The catalytically active paste was prepared by mechanically mixing (e.g., by stirring) the catalyst powder, i.e., for example, the mixed-metal oxide powder, the zeolite and optional additives, for example with a cellulose-based binder.

[0139] The binder was prepared by mixing for 20 minutes, using a propeller stirrer, 16 g of ethylcellulose (Merck) in 422 g of terpineol (i.e., p-menth-1-en-8-ol). 32 g of catalyst and optional additives which increase the conductivity were then initially mixed, into 22 g of the binder, by hand, with a spatula, then further mixed using a 3-roll mill (Netzsch). The paste produced thereby was then collected in a 50 ml bottle.

[0140] This paste was then printed onto the electrolyte layer using a screen-printing device (DEK) using a screen with a mesh size of 53. Finally, the catalytically active layer was sintered at 400°C . for one hour.

[0141] 1. Catalytic Oxidation of Benzene (Comparative Example)

[0142] Various porous catalytic films having a BET surface area of $16\ \text{m}^2/\text{g}$ were screen printed on a $200\ \mu\text{m}$ electrolyte film of CeO_2 , then heat treated (see following table). Pt was then vapor-deposited on the electrolyte film as a counter-electrode. The reaction temperature was 450°C . A mixture of 5% benzene, 5% oxygen and 90% nitrogen was passed over the positive electrode at a rate of 2 l/h. Air was passed over the negative electrode at the same rate. No current was applied to the electrodes of the cell, and oxygen transfer from the negative electrode to the positive electrode was either substantially suppressed or not evident.

[0143] Results

Positive electrode material (catalytic film)	Phenol formation [mmol/h*g]
MoO ₃	0
Mo _{0.57} Bi _{0.86} Fe _{6.4} Co _{3.2} K _{0.05} oxide	0
Mo _{0.12} Bi _{0.5} Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 10% by weight of CeO ₂ plus 30% by weight of zeolite ZSM-5	0
Mo _{0.12} Bi ₅ Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 40% by weight of zeolite ZSM-5	0

[0144] 2. Electrocatalytic Oxidation of Benzene (According to the Present Invention)

[0145] Various porous catalytic films (see following table) having a BET surface area of 16 m²/g were screen printed on a 200 μm electrolyte film of CeO₂, then heat treated. Pt was then vapor-deposited on the electrolyte film as a counter-electrode. The reaction temperature was 450° C. A mixture of 5% benzene, 5% oxygen and 90% nitrogen was then passed over the positive electrode at a rate of 2 l/h. Air was passed over the negative electrode at the same rate. The applied voltage on the cell for controlling the oxygen ion flow was 1 V.

[0146] Results

Positive electrode material (catalytic film)	Phenol formation [mmol/h*g]
MoO ₂	0
Mo _{0.57} Bi _{0.86} Fe _{6.4} Co _{3.2} K _{0.05} oxide	0
Mo _{0.12} Bi _{0.5} Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 10% by weight of CeO ₂ plus 30% by weight of zeolite ZSM-5	0.35
Mo _{0.12} Bi ₅ Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 40% by weight of zeolite ZSM-5	0

[0147] 3. Catalytic Oxidation of Benzene Using Dinitrogen Monoxide in the Starting-material Stream (Comparative Example)

[0148] Various porous catalytic films (see following table) having a BET surface area of 18 m²/g were screen printed on a 80 μm electrolyte film of La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O₂, then heat treated. Pt was then vapor-deposited on the electrolyte film as a counter-electrode. The reaction temperature was 395° C. A mixture of 5% benzene, 5% oxygen, 3% dinitrogen monoxide and 87% nitrogen was then passed over the positive electrode at a rate of 2 l/h. Air was passed over the negative electrode at the same rate. No current was applied to the electrodes of the cell, and oxygen transfer from the negative electrode to the positive electrode was either substantially suppressed or not evident.

[0149] Results

Positive electrode material (catalytic film)	Phenol formation [mmol/h*g]
MoO ₃	0
Mo _{0.57} Bi _{0.86} Fe _{6.4} Co _{3.2} K _{0.05} oxide	0
Mo _{0.12} Bi _{0.5} Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 10% by weight of CeO ₂ plus 30% by weight of zeolite ZSM-5	0.5
Mo _{0.12} Bi ₅ Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 40% by weight of zeolite ZSM-5	0.10

[0150] 4. Electrocatalytic Oxidation of Benzene Using Dinitrogen Monoxide in the Starting-material Stream (According to the Present Invention)

[0151] Various porous catalytic films (see following table) having a BET surface area of 18 m²/g were screen printed on a 80 μm electrolyte film of La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O₂, then heat treated. Pt was then vapor-deposited on the electrolyte film as a counter-electrode. The reaction temperature was 395° C. A mixture of 5% benzene, 5% oxygen, 3% dinitrogen monoxide and 87% nitrogen was passed over the positive electrode at a rate of 2 l/h. Air was passed over the negative electrode at the same rate. The applied voltage on the cell for controlling the oxygen ion flow was 1 V.

[0152] Results

Positive electrode material (catalytic film)	Phenol formation [mmol/h*g]
MoO ₃	0
Mo _{0.57} Bi _{0.86} Fe _{6.4} Co _{3.2} K _{0.05} oxide	0
Mo _{0.12} Bi _{0.5} Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 10% by weight of CeO ₂ plus 30% by weight of zeolite ZSM-5	2.10
Mo _{0.12} Bi ₅ Fe ₄ Co ₈ Ca _{0.1} K _{0.1} oxide plus 40% by weight of zeolite ZSM-5	0.95

[0153] The priority document of the present application, German patent application 100 26 940.0 filed May 30, 2000, is incorporated herein by reference.

[0154] Obviously, numerous modifications and variations on the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and is intended to be secured by Letters Patent is:

1. An electrochemical cell comprising a negative electrode, a solid electrolyte which conducts oxygen ions, a positive electrode comprising a positive electrode material comprising at least one material selected from the group consisting of a zeolite, a mordenite, a silicate, a phosphate, and a mixed-metal oxide, and a power source connected to the positive and negative electrode, wherein said positive electrode material has a pore size of less than 200 nm.

2. The electrochemical cell of claim 1, wherein the positive electrode material is a coating.

3. The electrochemical cell of claim 1, wherein the negative electrode and positive electrode are disposed on opposing surfaces of the solid electrolyte.

4. The electrochemical cell of claim 1, wherein the positive electrode material comprises a compound of formula IV



wherein

E1=an element from group IA, IIA, IIIA, IVA or VA or IIIB, IVB, VB, VIB, VIIB or VIII of the Periodic Table of the Elements

α=from 0 to 0.1,

β=from 0 to 0.1,

with the proviso that α and β are not simultaneously 0.

5. The electrochemical cell of claim 1, wherein the pore size of the positive electrode material is less than 20 nm.

6. The electrochemical cell of claim 1, wherein the solid electrolyte which conducts oxygen ions comprises cerium oxide (CeO₂) or cerium oxide (CeO₂) stabilized with at least one compound selected from the group consisting of lanthanum oxide (La₂O₃), yttrium oxide (Y₂O₃), ytterbium oxide (Yb₂O₃) and gadolinium oxide (Gd₂O₃).

7. The electrochemical cell of claim 1, wherein the solid electrolyte which conducts oxygen ions comprises zirconium oxide (ZrO₂) or zirconium oxide (ZrO₂) stabilized with at least one compound selected from the group consisting of calcium oxide (CaO), scandium oxide (Sc₂O₃), yttrium oxide (Y₂O₃) and ytterbium oxide (Yb₂O₃).

8. The electrochemical cell of claim 1, wherein the solid electrolyte which conducts oxygen ions comprises a metal or metal oxide.

9. The electrochemical cell of claim 1, wherein the solid electrolyte which conducts oxygen ions comprises a perovskite of formula II



wherein

Ln=La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu

X¹=Ca, Sr, Ba and/or Mg

X²=Ga, Al, Mn, Ti, Nb, Y, W and/or Zr

X³=Fe, Co, Ni and/or Cu

a=0.1 to 0.9,

b=0.1 to 0.9,

c=0 to 0.9,

d=0 to 0.9

with the proviso that a+b=0.3 to 1.5.

10. The electrochemical cell of claim 1, wherein the solid electrolyte which conducts oxygen ions comprises a pyrochloro compound of formula III



wherein

Ln=La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu

X⁴=Na, Mg, Ca and/or Sr,

X⁵=Ti, Nb, Ta and/or Zr,

X⁶=Fe, Al, Sc, Ga and/or Y,

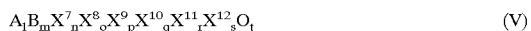
f=0.2 to 1.2,

g=0 to 0.8,

h=0.2 to 1.2,

i=0 to 0.8.

11. An electrochemical cell of claim 1, wherein the positive electrode material comprises a mixed oxide of formula V



wherein

A and B are an element from Group IA, IIA and/or VA and/or Group IVB, VB, VIB, VIIB, or VIII of the Periodic Table of the Elements

X⁷=V, Nb, Cr, W, Ta, Ga and/or Ce

X⁸=Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr and/or Ba,

X⁹=La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cu, Ag, Au, Pd and/or Pt,

X¹⁰=Fe, Co, Ni and/or Zn,

X¹¹=Sn, Pb, Sb and/or Te,

X¹²=Ti, Zr, Si and/or Al, where

l=0.001 to 30,

m=0.001 to 20,

n=0 to 15,

o=0.001 to 10,

p=0 to 10,

q=0 to 40,

r=0 to 10, and

s=0 to 80, with the proviso that l+m is ≥0.01 and l+o is ≥0.005.

12. The electrochemical cell of claim 1, wherein the positive electrode further comprises a mixture of the solid electrolyte which conducts oxygen ions and the positive electrode material.

13. The electrochemical cell of claim 1, wherein the positive electrode further comprises a mixture of an electrically conductive metal and the positive electrode material.

14. The electrochemical cell of claim 1, wherein a metal foil having a maximum thickness of 200 μm is disposed between the solid electrolyte which conducts oxygen ions and the positive electrode.

15. The electrochemical cell of claim 14, wherein the metal foil comprises at least one metal selected from the group consisting of Cu, Au, Ag, Pt, Pd and Ir.

16. The electrochemical cell of claim 1, wherein the negative electrode comprises a metal.

17. The electrochemical cell of claim 1, wherein the negative electrode comprises at least one metal selected from the group consisting of Cu, Au, Ag, Pt, Pd, and Ir.

18. The electrochemical cell of claim 1, wherein the negative electrode comprises one or more metal oxides or a metal mixed oxide.

19. The electrochemical cell of claim 1, wherein the negative electrode comprises a perovskite of the general formula I



wherein

X¹³=Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu,

X¹⁴=Ca, Sr, Ba and/or Mg,

X¹⁵=Mn, Fe, Ti, Ga, Mn and/or Zr,

X¹⁶=Co, Ni, Cu, Al and/or Cr

u=0 to 0.2,

v=0 to 1.0,

w=0.01 to 0.8,

with the proviso that u+v+w is ≤ 1.5 , and

x=0.2 to 1.3,

y=0 to 0.9,

with the proviso that x+y is ≥ 0.3 .

20. A process for the selective oxidation of an organic compound in an electrochemical cell, comprising:

passing the organic compound over the surface of a positive electrode comprising a positive electrode material comprising at least one material selected from the group consisting of a zeolite, a mordenite, a silicate, a phosphate, and a mixed-metal oxide having a pore size of less than 200 nm, thereby partially oxidizing the organic compound,

passing an oxygen- or N₂O-containing gas over a negative electrode,

wherein a solid electrolyte which conducts oxygen ions is disposed between the positive and negative electrodes, and the positive and negative electrodes are connected to a power source.

21. The process of claim 20, wherein the positive electrode material comprises a compound of formula IV



wherein

El=an element from group IA, IIA, IIIA, IVA or VA or IIB, IVB, VB, VIB, VIIB or VIII of the Periodic Table of the Elements

α =from 0 to 0.1

β =from 0 to 0.1,

with the proviso that α and β are not simultaneously 0.

22. The process of claim 20, wherein the pore size of the positive electrode material is less than 20 nm.

23. The process of claim 20, wherein the solid electrolyte which conducts oxygen ions comprises cerium oxide (CeO₂) or cerium oxide (CeO₂) stabilized with at least one stabilizer selected from the group consisting of lanthanum oxide (La₂O₃), yttrium oxide (Y₂O₃), ytterbium oxide (Yb₂O₃) and gadolinium oxide (Gd₂O₃).

24. The process of claim 20, wherein the solid electrolyte which conducts oxygen ions comprises zirconium oxide (ZrO₂) or zirconium oxide (ZrO₂) stabilized with at least one stabilizer selected from the group consisting of calcium oxide (CaO), scandium oxide (Sc₂O₃), yttrium oxide (Y₂O₃) and ytterbium oxide (Yb₂O₃).

25. The process of claim 20, wherein the solid electrolyte which conducts oxygen ions comprises a metal or metal oxide.

26. The process of claim 20, wherein the solid electrolyte which conducts oxygen ions comprises a perovskite of formula II



wherein

Ln=La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu

X¹=Ca, Sr, Ba and/or Mg

X²=Ga, Al, Mn, Ti, Nb, Y, W and/or Zr

X³=Fe, Co, Ni and/or Cu

a=0.1 to 0.9,

b=0.1 to 0.9,

c=0 to 0.9,

d=0 to 0.9

with the proviso that a+b=0.3 to 1.5.

27. The process of claim 20, wherein the solid electrolyte which conducts oxygen ions is a pyrochloro compound of formula III



wherein

Ln=La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu

X⁴=Na, Mg, Ca and/or Sr,

X⁵=Ti, Nb, Ta and/or Zr,

X⁶=Fe, Al, Sc, Ga and/or Y,

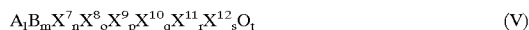
f=0.2 to 1.2,

g=0 to 0.8,

h=0.2 to 1.2,

i=0 to 0.8.

28. The process of claim 20, wherein the positive electrode material comprises a mixed oxide of formula V



wherein

A and B are an element from Group IA, IIA and/or VA and/or Group IVB, VB, VIB, VIIB, or VIII of the Periodic Table of the Elements

X⁷=V, Nb, Cr, W, Ta, Ga and/or Ce

X⁸=Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr and/or Ba,

X⁹=La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cu, Ag, Au, Pd and/or Pt,

X¹⁰=Fe, Co, Ni and/or Zn,

X¹¹=Sn, Pb, Sb and/or Te,

X¹²=Ti, Zr, Si and/or Al, where

l=0.001 to 30,

m=0.001 to 20,

n=0 to 15,

o=0.001 to 10,

p=0 to 10

q=0 to 40

r=0 to 10 and

s=0 to 80, with the proviso that l+m is ≥ 0.01 and l+o is ≥ 0.005 .

29. The process of claim 20, wherein the positive electrode further comprises a mixture of the solid electrolyte which conducts oxygen ions and the positive electrode material.

30. The process of claim 20, wherein the positive electrode further comprises a mixture of an electrically conductive metal and the positive electrode material.

31. The process of claim 20, wherein a metal foil having a maximum thickness of 200 μm is disposed between the solid electrolyte which conducts oxygen ions and the positive electrode.

32. The process of claim 31, wherein the metal foil comprises at least one metal selected from the group consisting of Cu, Au, Ag, Pt, Pd and Ir.

33. The process of claim 20, wherein the negative electrode comprises a metal.

34. The process of claim 20, wherein the negative electrode comprises at least one metal selected from the group consisting of Cu, Au, Ag, Pt, Pd, and Ir.

35. The process of claim 20, wherein the negative electrode comprises one or more metal oxides or a mixed metal oxide.

36. The process of claim 20, wherein the negative electrode comprises a perovskite of formula I



wherein

X¹³=Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu,

X¹⁴=Ca, Sr, Ba and/or Mg,

X¹⁵=Mn, Fe, Ti, Ga, Mn and/or Zr,

X¹⁶=Co, Ni, Cu, Al and/or Cr

u=0 to 1.2,

v=0 to 1.0

w=0.01 to 0.8,

with the proviso that u+v+w is ≤1.5

x=0.2 to 1.3,

y=0 to 0.9,

with the proviso that x+y is ≥0.3.

37. An electrochemical cell comprising a negative electrode means, a positive electrode means, an electrolyte means capable of conducting oxygen ions therebetween, and means for applying a voltage to the positive and negative electrode means.

38. A process for the selective oxidation of an organic compound in an electrochemical cell, comprising:

passing the organic compound over the surface of a positive electrode comprising a positive electrode material, whereby the organic compound is partially oxidized,

passing an oxygen- or N₂O-containing gas over a negative electrode, whereby the oxygen or N₂O is converted to oxygen ions,

wherein the oxygen ions are conducted in an ion conductive means disposed between the positive and negative electrodes, and the positive and negative electrodes are connected to a means for applying a voltage to the positive and negative electrode.

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